Russian Chemical Reviews, Volume 53 (1984)

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Russian Chemical Reviews

January 1984

Translated from *Uspekhi Khimii*, 53, 3-39 (1984)

U.D.C. 547.64

The Present State and Prospects for the Development of the Field of Polycondensation

V.V.Korshak

The aim of the review is to survey and examine data obtained in recent years and characterising the progress in the field of the synthesis of polymers by polycondensation methods. The rule of functionality is shown to have limited applicability and a new formulation, taking into account the structure of the monomers and the reaction conditions, is proposed.
It is also shown that the rule of the non-equivalence of the functional groups does not hold solely in equilibrium polycondensation reactions and that the polymers obtained by polycondensation methods are of the heterounit type. The ways in which anomalous units are formed and the influence of the heterounit structure on the set of properties of the polymer synthesised have been established. Data on the kinetics and mechanism of non-equilibrium polycondensation are considered.
The great importance of catalysis in polycondensation reactions as one of the most significant factors governing progress in this field is demonstrated. Methods for the synthesis of conformationally regular polymers have been discovered by studying acceptor-catalytic polycondensation.
A significant influence of solvents on polycondensation processes has been demonstrated. The characteristic features of joint polycondensation involving non-equilibrium reactions, the prospects for the further development of polycondensation processes, and the possible future of polymers obtained in this way are examined.
The bibliography includes 215 references.

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I. INTRODUCTION

The field of polycondensation has been developing at a rapid rate at the present time and the manufacture of polymers obtained by polycondensation methods has been expanding. The development of research into processes involving the synthesis of polymers by polycondensation methods has enriched polymer science in polymer formation reactions and numerous new polymers and has made it possible to understand the mechanism of polycondensation processes[1].

The aim of the present review is to indicate the advances made at the present time in the polycondensation methods for the synthesis of polymers. Clearly it is quite impossible to describe the development of this enormous field within the framework of a single article. Recognising this, the author's aim was to attempt the more modest task of demonstrating in relation to individual examples the advances made in this field and of indicating the principal trends in the development of polycondensation synthesis.

Since the time when Berzelius proposed the concept of polymers and Gay-Lussac and Pelouze obtained the first synthetic polyester by the polycondensation of a hydroxy-acid, 150 years have elapsed[2]. This was followed by the publication of communications concerning the syntheses of various polymers by polycondensation processes. Thus Liebig[3] obtained an acetaldehyde resin in 1835, Berzelius[4] synthesised the first branched polyester in 1847, and Butlerov[5] obtained polyformaldehyde in 1859 by the condensation of methylene iodide. In 1872 Bayer[6] achieved for the first time the synthesis of a phenol-formaldehyde polymer, which served as the basis for studies by many investigators. In 1909–1912 Baekeland[7] and Petrov[8] created on this basis the manufacture of phenol-formaldehyde polymers (bakelite and carbolite).

The studies by Carothers[9] on the polycondensation of dicarboxylic acids with diamines and glycols constituted an important stage in the development of polycondensation. The discovery of polysiloxanes by Andrianov in 1937 [10] led to the appearance of a new branch of polycondensation, namely the synthesis of polymers with inorganic main molecular chains[11]. In subsequent years there was a growth of the number of studies in the field of polycondensation[1,12–15].

Table 1 lists the names of individual types of polycondensation and the dates of their discovery.

Table 1. Polycondensation processes.

Name of reaction	Year of discovery	Refs.	Name of reaction	Year of discovery	Refs.
Equilibrium polyesterification	1833	[2]	Polyrecombination	1957	[22]
Polyamidation	1862	[16]	Oxidative polycondensation	1960	[23]
Phenol-aldehyde polycondensation	1872	[6]	Polycyclocondensation	1960	[24]
Polyazination	1889	[17]	Conformationally specific polycondensation	1960	[25]
Interfacial polycondensation	1898	[18]	Condensation polydisproportionation	1972	[26]
Polyheterocyclisation	1908	[19]			
Polycoordination	1953	[20]			
Acceptor-catalytic polycondensation	1956	[21]			

Thus one may note that polycondensation, as a fundamental synthetic process, has now provided science and technology with an enormous number of polymeric structures and has played an important role in the formulation of the fundamental ideas of polymer science[12–15]. It must be emphasised that it is also very important as a method of synthesis of natural polymers, because many of the most important biopolymers such as proteins, nucleic acids, natural rubber, cellulose, starch, glycogen, chitin, pentosans, and many others, as well as enzymes and hormones are evidently formed in living organisms via various polycondensation processes[1].

II. INDUSTRIAL PRODUCTION OF POLYCONDENSATION POLYMERS

The role of polycondensation in industry is now very considerable. It needs to be said that in general the plastics industry arose in its time as an industry based on the employment of polycondensation processes and only subsequently polymerisation processes began to develop to an increasing extent. The first synthetic industrial products were phenol-formaldehyde polymers synthesised in 1909–1912 by Baekeland and Petrov, after which glyptals and in 1920 carbamides were developed. Polymerisation polymers were produced on a large scale as early as the 1930's. At the present time polycondensation polymers also play a considerable role in the plastics and artificial fibres industry. Table 2 illustrates the world production of the most important polycondensation polymers[27–29]. It shows that the production of polycondensation polymers has doubled each 10 years. Data are listed only for the four leading polymers in this field, because the others, whose number is fairly large, make a much smaller contribution to industrial production. They include alkyd polymers, polycarbonates, polyarylates, epoxides, polyorganosiloxanes, poly(phenylene oxides), polyimides, etc. The polymers obtained by polycondensation methods occupy a fairly major place in the overall production of polymers.

Table 2. The world production of the most important polycondensation polymers (in thousands of tonnes).[27–29]

Name	Years		
	1960	1970	1980
Foam plastics	700	1600	2500*
Polycarbamides	600	2050	2560*
Polyamides	406	1897	3125
Polyesters	123	1643	5132
	1829	7190	13317
Total growth of production, %	100	393	728

*Data for 1979.

It needs to be said that, when polymers are subdivided into polymerisation and polycondensation types, one must always bear in mind the fact that such subdivision is to a large extent conventional not only as regards the meaning given to these terms but also because there exists at present an increasing group of polymers, which are obtained as a result of the simultaneous employment of polymerisation and polycondensation reactions. These include, for example, unsaturated polyesters, which are obtained in the first stage via polycondensation reactions, while in the last stage they are hardened by polymerisation processes involving their double bonds. Polyester urethanes are likewise obtained as polycondensation products in the first stage in the form of branched polyesters, which undergo joint polymerisation with di-isocyanates in the subsequent stage.

III. CERTAIN CHARACTERISTIC FEATURES OF POLYCONDENSATION

Polycondensation processes differ significantly from polymerisation processes. In the first place attention should be drawn to the greater universality of polycondensation

processes and the wide variety of the structures which can be obtained with their aid. The structures obtained by polymerisation processes are less varied. Among polycondensation polymers, there is a large group of polymers distinguished by a high thermal stability and strength, electrically conducting polymers, physiologically active polymers, etc.

It can be assumed that approximately 25000, i.e. one half, of the papers published annually and describing the synthesis of new polymers deal with polymers obtained by polycondensation[15]. Finally, yet another of the most important differences consists in the fact that these two processes differ greatly as regards the number of chemical reactions employed. In the case of polymerisation we are dealing virtually with two chemical processes: addition to a multiple bond between two atoms and addition to rings. On the other hand, several tens of chemical reactions are used in polycondensation at the present time and the number of such reactions increases each year. We have in addition a new but very promising field of polymer science involving inorganic polymers, which is almost entirely based on polycondensation, since the majority of heterochain inorganic polymers are obtained by polycondensation[30].

The same remark applies also to biopolymers, which are likewise obtained mainly by polycondensation methods[15].

After this brief description of the characteristics of polycondensation reactions, we shall deal with the present state of this field, attention being concentrated primarily on the characteristic features of polycondensation and the causes of the appearance of a heterounit structure, as well as the formation of a macromolecule, its kinetics and mechanism, and the influence of the process conditions, catalysts, and solvents on this reaction, i.e. the questions which at present determine the progress in the field of polycondensation.

Table 3. The equilibrium constants of certain equilibrium and non-equilibrium polycondensation reactions[12-14].

Reaction investigated	Starting materials	K_p
	Equilibrium polycondensation	
Polyesterification	Pentamethylene glycol + adipic acid	6.00
Polyamidation	ω-Aminoundecanoic acid	8.88
Polycoordination	Beryllium acetylacetonate + 4,4'-di-(acetoacetylphenyl) ether	4.00
	Non-equilibrium polycondensation	
Polyesterification	Dian + 2,2-di(4-hydroxyphenyl)propane diformate	$4.74 \cdot 10^3$
Esterification	Phenol + benzoyl chloride	$4.48 \cdot 10^3$
Polycyclisation	Dihydrazide of di(carboxyphenyl) ether + dichloride of di(carboxyphenyl) ether	$1 \cdot 10^{25}$
Polyamidation	Pyromellitic acid dianhydride + aminophenyl) ether	$1 \cdot 10^5$

IV. EQUILIBRIUM AND NON-EQUILIBRIUM POLYCONDENSATION

The study of the characteristic features of polycondensation processes led the present author to the conclusion that all the known polycondensation reactions can be combined into two large groups known as (1) equilibrium and (2) non-equilibrium polycondensation[12-15,31,32]. The difference between them is determined mainly by the equilibrium constant of the given process. Equilibrium polycondensation involves reactions whose equilibrium constants are below 10^3 ($K_e < 10^3$), while reactions whose equilibrium constants are above 10^3 ($K_e > 10^3$) belong to non-equilibrium polycondensation[15,33-35]. Table 3 presents examples of reactions of both types.

Equilibrium polycondensation and its features have been studied in greater detail[12,14,15,33]. These two types of polycondensation processes also differ as regards the properties of the polymers formed, the reaction mechanism, the nature and mechanism of the action of the catalysts, kinetics, molecular weight distribution, the mechanism of joint polycondensation, the structure of copolymers, and other characteristic features of these processes, which will be considered below[32-35].

Non-equilibrium polycondensation has been studied in less detail and this factor necessitates a detailed investigation of the laws controlling its course. The importance of this field is due to the fact that non-equilibrium polycondensation actually makes it possible to synthesise polymers at a higher rate and to obtain high-molecular-weight polymers with new structural units and an interesting set of physical and chemical properties[13,14,15,34,36,37].

V. THE FUNCTIONALITY OF THE STARTING MATERIALS

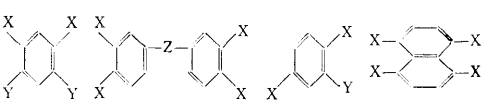
The functionality of the starting materials is one of the fundamental concepts in the field of polycondensation[38-47,143]. Kienle was the first to draw attention to this concept and emphasised its importance in processes involving the formation of three-dimensional network polymers[42].

Carothers[9] formulated the rule of the functionality of the initial monomers, pointing out that linear polymers are formed when the initial monomers are bifunctional. On the other hand, if their functionality is three and more, gel formation takes place and a three-dimensional insoluble and infusible polymer is produced. This is expressed by the relation $P = 2/f$, where P is the degree of reaction and f the functionality, i.e. the number of functional groups in the monomer molecule.

In the case of a bifunctional monomer $P = 1$, which leads to the formation of a linear polymer. For a trifunctional monomer, $P = 2/3$ and for a tetrafunctional one, $P = 1/2$, which implies the formation of three-dimensional polymers, i.e. a gel.

Subsequently many investigators turned their attention to problems of functionality and attempted to find the most effective forms of the expression for functionality and for the application of this concept to polycondensation processes[38-47].

In the course of the development of polymer science, an increasing number of instances have been observed in which the Carothers rule was not confirmed and tri- and tetrafunctional monomers proved capable of forming polymers with linear macromolecules[31,47]. The formation reactions of various polyheteroarylenes, in which tetrafunctional compounds such as tetramines, dihydroxydiamines, tetracarboxylic acids, diaminodicarboxylic acids, and similar compounds having the general formula



are used, may serve as examples. In this case the mutual arrangement of the functional groups is decisive. For an

arrangement of the functional groups which permits the formation of five- or six-membered rings, linear macromolecules of heterocyclochain polymers are obtained. This demonstrates the possibility of the formation of linear polymers made up of tri- and tetra-functional monomers, which had been previously regarded as impossible[38,47]. One must therefore conclude that not only the overall functionality of the initial monomers but also the corresponding favourable mutual arrangement of the functional groups in the unit or the initial monomers is important for the foration of linear polymers. This enabled the author to reformulate the question of the importance of the functionality of the monomers in non-equilibrium polycondensation[15,47] and to put forward a different treatment of the concept of functionality[1,15,38,47]. Functionalities of three types, designated as possible (Φ_p), practical (Φ_{pr}), and relative (Φ_r) functionalities, were proposed[47]. The possible functionality is defined as the total number of functional groups of all types contained in the monomer or oligomer molecule. The practical functionality is defined as the number of functional groups involved in the polycondensation process in the formation of bonds between the constituent units of the polymer, while the relative functionality represents the ratio of the possible and practical functionalities and is given by the equation $\Phi_r = \Phi_p/\Phi_{pr}$. The relative functionality characterises the difference between the reactivities of the reacting monomers and oligomers.

If questions of functionality are considered from the standpoint of its dependence on the structure of the monomers, then the monomers can be divided into two large groups: normal and anomalous monomers. The normal monomers obey the Carothers rule, while the anomalous monomers do not. Accordingly, the possible functionality of the normal monomers is somewhat greater than their practical functionality:

$$\Phi_p > \Phi_{pr},$$

which means that the relative functionality is greater than unity:

$$\Phi_r > 1.$$

The difference between the possible and practical functionalities

$$\Phi_p - \Phi_{pr} = \Phi_{ap}$$

represents the active possible functionality (Φ_{ap}), which determines the possibility of further growth of the molecule. Accordingly, linear polymers are formed when $\Phi_p = 2$. Three-dimensional polymers are produced when the active possible functionality is greater than two:

$$\Phi_{ap} > 2.$$

The questions involving the formation of cyclic groups are then of secondary importance, although cyclic groups of different size are formed in the synthesis of three-dimensional network polymers, which ultimately leads to a three-dimensional network construction, i.e. to a gel point[1,48–52]. It has been noted that the gel point depends on the flexibility of the polymer molecules and on the concentration of the polymer in solution[48]. One must therefore conclude that not only the overall functionality of the initial monomers but also the corresponding favourable mutual *ortho*-arrangement of the functional groups in the unit or in the initial monomers, i.e. the so-called "*ortho*-effect", is important for the formation of linear polymers.

VI. THE RULE OF THE NON-EQUIVALENCE OF FUNCTIONAL GROUPS

The rule of the non-equivalence of the functional groups is known to be valid in all instances of polycondensation where the starting materials are bifunctional[53]. The molecular weight of the polymers produced in the equilibrium polycondensation reaction is regulated on the basis of this principle by adding different amounts of monofunctional substances or an excess of one of the initial monomers. Fig.1 illustrates this relation for equilibrium polycondensation[53]. Its investigation in non-equilibrium polycondensation for starting materials with a higher functionality showed that here too the excess of one of the starting materials has in most cases an analogous influence in the reactions of tetrafunctional monomers, which leads to a decrease of the molecular weight in proportion to the excess of one of the initial monomers. Such a relation has been observed in many instances of non-equilibrium polycondensation. Fig.2 illustrates the dependence of the viscosity of the solution of the polyimide formed on the excess of the starting materials in the reaction of a diamine with pyromellitic acid dianhydride[54]. Fig.3 shows that the reaction of a diamine with the dichloride of *m*-carbaboranedicarboxylic acid is also very sensitive to the excess of the starting materials[55].

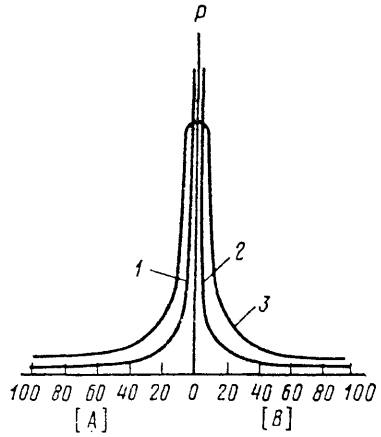


Figure 1. Dependence of the polymerisation coefficient *P* of the polymer obtained by the polycondensation reaction on the excess of the starting materials A and B: *1*) and *2*) calculated; *3*) experimental.

In general, the reactions of different tetrafunctional nucleophiles with tetracarboxylic acids or their derivatives obey the rule of the non-equivalence of the functional groups, as shown in a general form in Fig.4.[56]

Thus the examples presented demonstrate fairly clearly a distinct dependence of the molecular weight (MW) of the polymer synthesised on the excess of one of the initial monomers also in the case of tetrafunctional monomers and hence the "rule of the non-equivalence of the functional groups" remains in force and also in relation to polyfunctional monomers in non-equilibrium polycondensation[53].

The possibility of the acceleration of the concluding stage of the non-equilibrium polycondensation reaction as a result of the introduction of monomers with more reactive functional groups than the terminal groups has been demonstrated and it has been shown that the maximum attainable molecular weight of the polymer depends on the stoichiometric composition of the reaction mass and on the relative reactivities of the functional groups of the monomer[57].

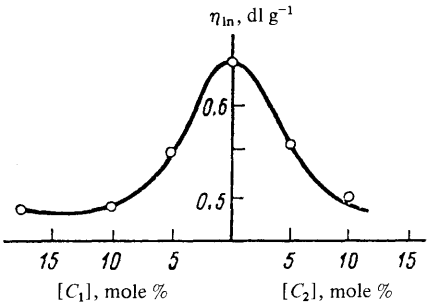


Figure 2. Dependence of η_{ln} for a solution of anilinephthalein polypyromellitimide on the ratio of the starting materials; c_1 = dianhydride concentration; c_2 = diamine concentration.

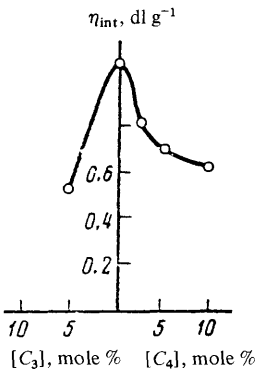


Figure 3. The influence of the ratio of the starting materials on η_{int} for 0.5% solutions of polyamido-*m*-carbaborane in DMF; c_3 = diamine concentration; c_4 = acid chloride concentration.

VII. THE HETEROUNIT STRUCTURE OF THE POLYMERS FORMED IN NON-EQUILIBRIUM POLYCONDENSATION PROCESSES

Heterounit polymers are produced in the non-equilibrium polycondensaton reaction as a result of the formation of anomalous units in the set of polycondensation reactions, illustrated in Fig.5.[58-61]

The anomalous units formed under these conditions differ in their structure from the main units of the macromolecule.

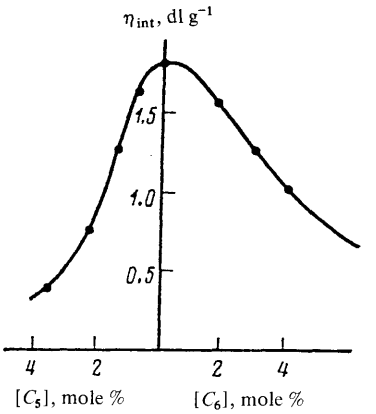
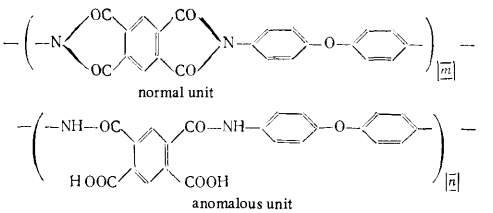


Figure 4. The influence of the excess of the starting materials on the viscosities of solutions of polymers obtained from various tetrafunctional monomers (dicarboxylic acid dihydrazides, bis-o-aminophenols, dianilinodiamines, and bisanthranilic acid diamides) by reaction with polycarboxylic acids; c_5 = nucleophile concentration; c_6 = electrophile concentration.

The formation of the anomalous units generates the so-called "heterounit" polymers[14,36,58,62-66]. The present author suggested that the structure of the heterounit polymers be expressed by the general formula

$$-[-(-M-)_{\boxed{m}}-(-A-)_{\boxed{n}}-]_x- \ ,$$

where M is the normal unit, A the anomalous unit, and the coefficients $\boxed{m}$ and $\boxed{n}$ denote the statistical distribution of the M and A units. The real formula of the polymers such as, for example, polyimide is therefore as follows:



In this case the anomalous units are those in which ring closure has not taken place. In other instances there is a possibility of side reactions of different character, as shown in Fig.5. The presence of the anomalous units has a significant influence on the entire set of the chemical and physical properties characteristic of the given polymer[58,63,67-69]. The study of the conditions leading to the formation of the anomalous units and hence to the appearance of heterounit polymers is one of the most important tasks in synthetic polymer chemistry, since without it it is impossible to understand and explain fully the dependence of the properties of the polymers on their structure[14,36,58,62-66]. The presence of anomalous units of different kinds has been demonstrated for many classes of polymers obtained by polycondensation methods[15,62]. These include representatives of polyamides[70], polyesters[71], polycarbonates[81], unsaturated polyesters[72], polyarylates[73,74], polybenzimidazoles[75], pyrrones[76], and polyimides[77,78]. The presence of non-cyclised and anomalous structures in polybenzoxazoles[79], polyquinoxalines[80], polytriazines[81], squaric acid polyamides[82], polysulphones[83], and other polymers[84] has been established recently. To complete

the picture, one should add that anomalous units are present also in polymers obtained by polymerisation methods from monomers and by the modification of polymers[63,64,85].

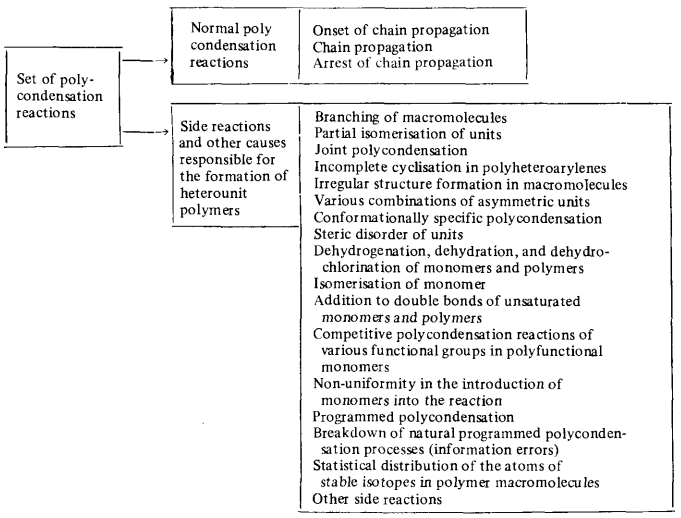
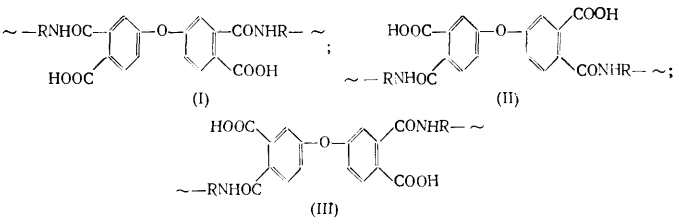


Figure 5. The set of polycondensation reactions.

Finally isotopes are a significant factor in the formation of heterounit structures. The point is that all organogenic elements from which the majority of polymers are constructed each have several stable and radioactive isotopes. Stable isotopes forming part of the composition of the polymers are distributed statistically in their macromolecules and each macromolecule therefore has a structure different from that of the others. This naturally affects the properties of the polymers, as shown in relation to deuterated polyethylene[65]. The substitution of hydrogen by deuterium in polyethylene results in an appreciable alteration of physical characteristics such as density, melting point, glass point, yield point, and chemical properties. This led to the conclusion that the presence of isotopes in macromolecules promotes the acquisition of a heterounit structure by polymers[40,41,86,87]. At the same time account must be taken of the possibility of the combination of a series of effects and the simultaneous operation, together with the isotope effect, of factors such as branching, isomerisation, etc. The influences of these effects may coincide and enhance one another.

The heterounit structure should be manifested particularly significantly in the case of biopolymers, where one may expect extremely specific and very marked manifestations of the isotope effect. In fact, we know that extremely small changes in the structures of substances such as proteins, nucleic acids, etc., have a significant influence on biological functions. At the same time it is known that different isotopes are non-equivalent as regards their physiological properties. Thus, among the causes responsible for the heterounit structure of polymers, one should include also the influence of stable isotopes in monomer and polymer molecules. Branching is a very special case in the heterounit structure of polycondensation products. It can arise as a result of various side reactions and owing to the use in the polycondensation reaction of starting materials with a functionality greater than two. For example, the addition of laproxid during the synthesis of poly(ethylene terephthalate) (lavsan) leads to the formation of a branched polyester[88].

The determination of the extent of the heterounit structure in polyamidoacids by ^{13}C NMR demonstrated the presence of three possible structures[89]:



The contents of these isomers vary within the following limits as a function of the nature of the solvent: (I) from a mole fraction of 0.33 to 0.46; (II) from 0.11 to 0.18; (III) from 0.43 to 0.49.

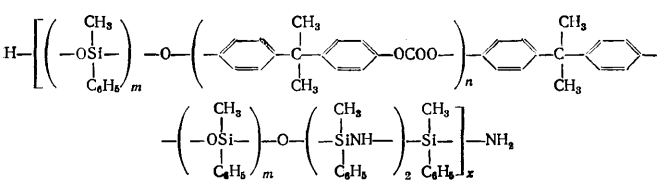
Since the presence of anomalous units in heterounit polymers influences significantly their chemical and physical properties, this factor must be taken into account in considering the relation between the structure and properties of polymers[14,44,50].

VIII. THE SYNTHESIS OF ORGANOELEMENTAL POLYMERS

An interesting feature of polycondensation processes is that this is in fact the main procedure whereby polymers containing different elements in the Periodic System are obtained. The usual organic polymers consist of elements such as carbon, hydrogen, oxygen, and nitrogen. The remaining elements are typical for organoelemental polymers. Polymers incorporating such elements, which are listed in Table 4, have now been obtained[37,40,41,86,87,90,91]. The table shows that there is a very great variety of organoelemental polymers obtained by polycondensation methods; 75 elements have already been incorporated in polymers of this kind. Evidently there is every reason to assume that further development of research into organoelemental polymers will enrich science and practical applications by a large number of new and interesting polymers.

New bonds between elements are formed in organoelemental polymers, imparting a new set of properties to the polymeric structures formed. Various heterobonds between the atoms constituting the polymer chain are presented in Table 5.

Among block copolymers, there exists an organoelemental block copolymer containing polycarbonate and polysilazasiloxane blocks having the following structure[92]:



IX. THE KINETICS AND MECHANISM OF THE POLYCONDENSATION REACTION

The kinetics of equilibrium polycondensation processes have been investigated in relation to a large number of examples[1,12,31,34,93]. However, many investigations devoted to

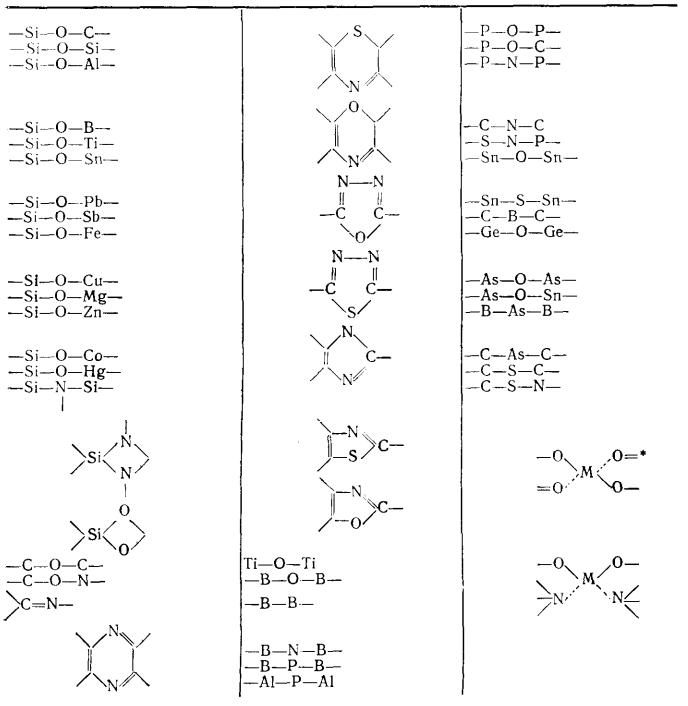
these problems are still being published. The kinetics of the non-equilibrium polycondensation reactions have been studied in less detail.

Table 4. Elements forming part of the composition of polymers obtained by polycondensation methods.

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

Lanthanides Ce Pr Sm Eu Gd Tb Dy Ho Fr Tu Yb Lu

Table 5. Linkages introduced into organoelemental polymers via polycondensation.



*M = Ca, Sr, Ba, Hg, Be, Fe, Ni, etc.

The successful investigation of the kinetics of the formation reaction of cardo-polymers has been possible by virtue of their solubility, since the starting materials employed are diamines with bulky substituents, such as, for example, anilinephthalein[94]. The introduction of polar groups into the polyimide unit with the aid of monomers of the type of di(3-amino-4-methoxyphenyl)methane has also made it possible to obtain soluble polymers and to investigate the process kinetics[61].

The study of the kinetics of the synthesis of polymers such as polyphenylquinoxalines[95], polyimides[96–98], polybenzoxazoles[97], polyoxadiazoles[99–101], polyarylates[102] and polyphenylenes[103] has likewise been described.

The kinetic curves for the reaction of terephthalic acid chloride with phenolphthalein in the presence of triethylamine are presented in Fig.6.[104] We see that the process is extremely rapid even at low temperatures.

It is of interest that the dependence of the viscosity of the polyarylate obtained on the reaction temperature is unusual and is expressed by a curve with two maxima, as shown in Fig.7.[102,105,106] This can be explained by the complex temperature dependence of the reaction rate constant[104,105].

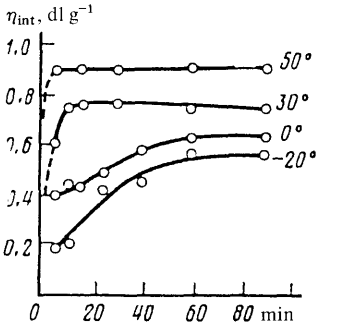


Figure 6. Variation of η_{int} of the polyarylate in the synthetic process.

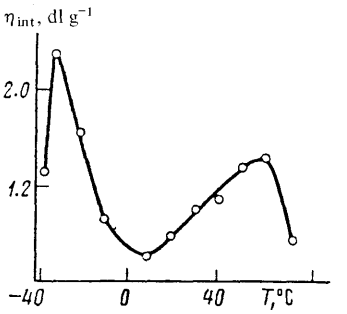


Figure 7. Temperature variation of η_{int} of the polyarylate.

Kuchanov[49] calculated the influence of the method of measuring out the monomers on the molecular weight distribution of the polymers obtained by non-equilibrium polycondensation and concluded that the number-average polycondensation coefficient is inversely proportional to the square root of the rate of introduction of the monomer.

In the single-stage synthesis of polyimide from pyromellitic anhydride and anilinephthalein in solution in nitrobenzene, the reaction should proceed as shown in Fig.8.[54] The yield of the polymer is then almost independent of the

reaction time, since the polymer is formed quantitatively after only 1 h.[107]

In the two-stage formation of polyoxadiazoles the second stage involves the closure of the heterocycle. Fig.9 presents curves describing the variation of the activation energy for the cyclisation of polyhydrazides[108]. The figure shows that an interesting feature of this process is the fact that the activation energy increases with increase of the degree of cyclisation, which is evidently associated with the increasing rigidity of the macromolecular chain and the steric hindrance to the heterocyclisation reaction.

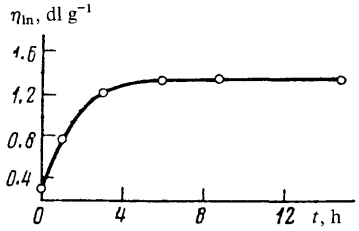


Figure 8. Dependence of η_{ln} of anilinephthalein polypyromellitimide on the reaction time.

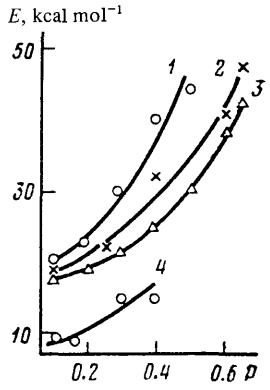
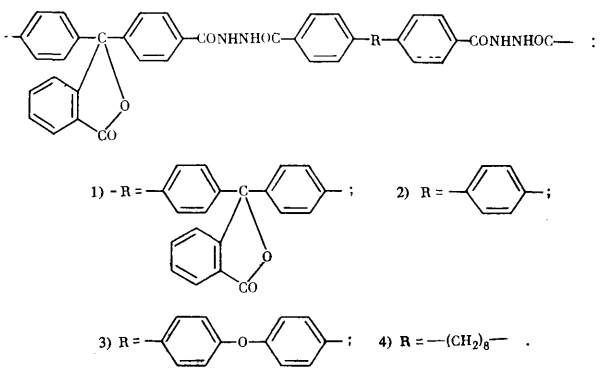


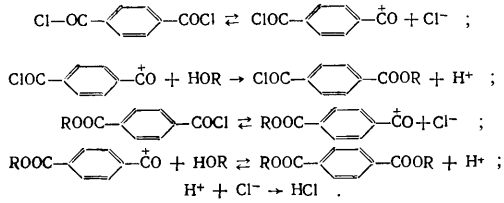
Figure 9. Dependence of the activation energy E for heterocyclisation on the degree of reaction P of the polyhydrazide having the general formula



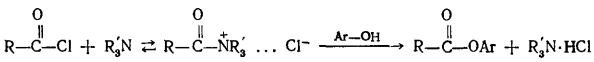
It has been found that the order in which the starting materials are mixed in the non-equilibrium polycondensation reaction has a considerable influence on the structure of the polymer formed when asymmetric monomers are used[109].

It is noteworthy that the mechanisms of various kinds of polycondensation reactions have been elucidated in detail only in a small number of instances. The mechanism of non-equilibrium polycondensation has been studied mainly in relation to polycondensation in solution[13,110].

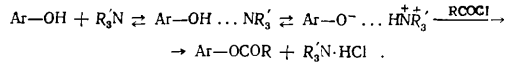
The study of the high-temperature non-equilibrium polycondensation of dicarboxylic acid chlorides with bisphenols in solution led to the conclusion that the reaction proceeds via an ionic mechanism in accordance with the equations[111,112]



The study of non-equilibrium polycondensation in solution in relation to the acceptor-catalytic polyesterification in the presence of tertiary amines led to the conclusion that the reaction can involve both the nucleophilic catalytic mechanism

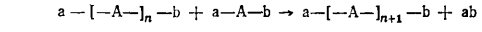


and the general base catalytic mechanism

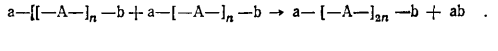


The particular pathway followed depends on the basicity of the tertiary amine and hence on its ability to form a hydrogen bond with phenol[113–116]. For a more basic amine, general base catalysis predominates[116].

An interesting feature of the polycondensation reaction is the possibility of its occurrence via two pathways, namely via the single-stage substitution



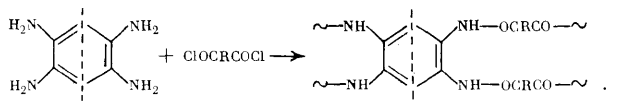
and via repeated dimerisation



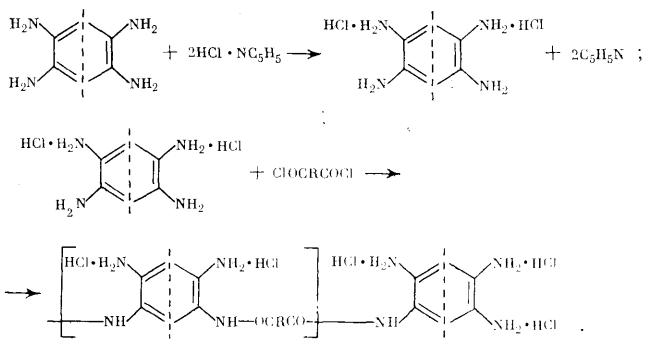
Evidently in practice both versions are realised, possibly with one of them predominating depending on the reaction conditions and the nature of the starting materials. It must be emphasised that this constitutes a significant difference between polycondensation processes and polymerisation in which there is no chain growth via repeated dimerisation.

Among the interesting results of the study of the mechanism of non-equilibrium polycondensation, mention must be made of a new procedure for the regulation of the structure of the macromolecule formed. It has been found that the addition of pyridinium chloride in the polycondensation of aromatic tetramines with carbaborane-*m*-dicarboxylic acid chloride makes it possible to obtain a linear polymer, while the reaction in the absence of this additive leads to the formation of a branched and cross-linked polyamide[117,118]. The reaction mechanism which explains the structure-regulating influence of pyridinium chloride is as follows: the reaction of the tetramine with the acid chloride gives

rise to a trimer:



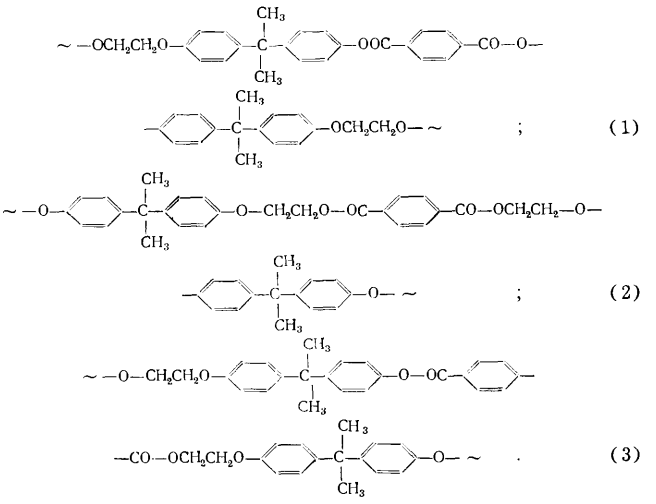
However, if pyridinium chloride is added, then the tetramine becomes bifunctional as a result of salt formation and a soluble linear polymer is therefore produced on treatment with the dicarboxylic acid dichloride:



Thus the amino-groups are neutralised, which prevents branching and terminates the growing chain at a specific reaction stage. An analogous pattern has also been observed in the reaction of bis(o-aminophenols) with acid dichlorides[66].

One of the important characteristics of polymers is the regularity of the structure of the polymer chain, which is particularly important for units with an asymmetric structure and determines the "head to tail", "head to head" and "tail to tail" dispositions.

The study of the acceptor-catalytic polycondensation of terephthalic acid chloride with the β-hydroxyethyl ether of 2,2-di(4-hydroxyphenyl)propane showed that, when the reaction is carried out under the usual conditions with the simultaneous introduction of the starting materials, a polymer with a statistical distribution of units is formed[119]. If the terephthalic acid chloride is added gradually to the reaction mixture, a difference in the reactivity of the hydroxyls is manifested and a polymer in which the "head to head" (1) and "tail to tail" (2) units predominate is obtained:



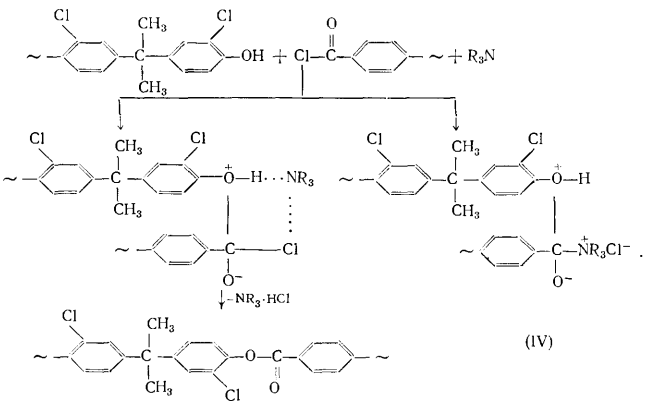
On the other hand, the "head to tail" configuration (3) is encountered more rarely. Thermodynamic methods have been recently applied on an increasing scale to the study of polycondensation processes. Thus a detailed investigation has been made of the thermodynamics of the synthesis of a series of polyheteroarylenes which led to the discovery of the temperature limits of the occurrence of the individual stages of the reaction and the thermodynamic functions of the polymers and the equilibrium constants of the process have been obtained, showing that the reactions are of the non-equilibrium polycondensation type[76,120]. Among the interesting approaches to the investigation of non-equilibrium polycondensation, mention must be made of the use of correlation analysis, whereby one can predict the reactivities of monomers with interdependent and independent reaction centres and calculate the rates of various polycondensation processes from the joint polycondensation constants[121].

A mechanism of the elementary stage in the polycondensation of diamines with pyromellitic anhydride postulating a consecutive electron and proton transfer in the electronically excited state of the complex formed by the reactant and solvent molecules has been proposed on the basis of the study of the phototransfer and thermal transfer of an electron[122].

X. CONFORMATIONALLY REGULAR POLYCONDENSATION

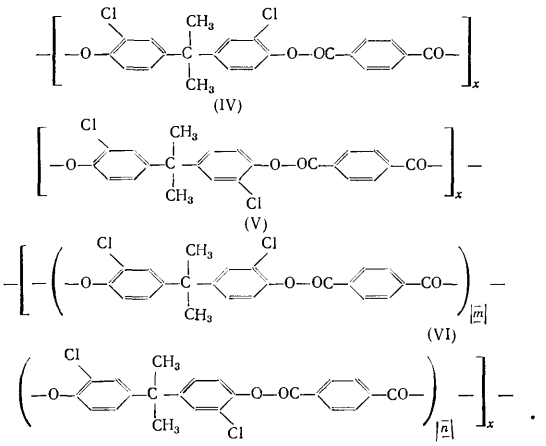
The study of the non-equilibrium polycondensation reaction in relation to the interaction of dicarboxylic acid chlorides with bisphenols in the presence of catalysts such as tertiary amines led to the formation of polyarylates whose properties differed depending on the reaction conditions and the nature of the catalysts.

The mechanism of the acceptor-catalytic polyesterification reaction occurring in this instance can be represented by the following scheme[123]:



In this case one can obtain a polyester containing two conformations of the units differing in the mutual arrangement of the halogen atoms. It has been shown for acceptor-catalytic polyesterification that the nature of the solvent and the catalyst plays a major role[25]. Thus the polycondensation of 2,2-di-(3-chloro-4-hydroxyphenyl)propane with terephthalic acid chloride leads to the formation of polyarylates with different properties, melting points, and solubilities depending on the reaction conditions[25,124]. The study of the polyarylates showed that they are conformationally regular polymers and consist of conformers with

different conformations, arising by virtue of hindered rotation[123,125]. They have the following structures:



(IV)

(V)

(VI)

Formulae (IV) and (V) represent two extreme structures: cisoid and transoid respectively. They can be regarded as analogues of the isotactic and syndiotactic structures of polyolefins. Formula (VI) corresponds to an atactic polymer containing both conformations, distributed in the polyarylate molecule either statistically or in blocks[126,127].

Similar polymers have also been obtained from other dian derivatives containing two methyl or two nitro-groups[128]. All such polymers evidently contain blocks made up of regularly distributed units. The size of the blocks depends on a number of factors and can vary within specific limits depending on the conditions of the synthesis and the nature of the solvent and the catalyst[123,125,127,129].

XI. THE MOLECULAR WEIGHT DISTRIBUTION IN THE POLYCONDENSATION PRODUCTS

The question of the molecular weight distribution in the polycondensation products has been studied in detail by a number of investigators[48,130,131]. It has now been established that, depending on the method of polycondensation, polymers with different molecular weight distribution functions are formed[131,132].

An interesting feature of the polycondensation in a solvent–precipitant system is the formation of polymers with a narrow molecular weight distribution (MWD). This is achieved by using solvents in which the polymer with chains having a length greater than the specified value P_C are insoluble[131].

The homogeneity of the reaction mass is also important for the MWD, since inhomogeneity leads to an increase of polydispersity[130]. Polycondensation yields products whose MWD can vary within wide limits. Thus, according to literature data, the polydispersity coefficient varies within wide limits ranging from 1 to 43.[32] Consequently there is no complete consistency with Flory's theory[133], according to which the polycondensation products must have the most probable distribution corresponding to a polydispersity of two. The non-equilibrium polycondensation of pyromellitic anhydride with di(4-aminophenyl) ether yielded polymers whose molecular weight distribution M_w/M_n varied from 1.53 to 3.72.[134,135] The narrower distribution can be explained by the fact that a helical conformation is products under the conditions of the synthesis, the degree of conversion into the helical form increasing when the MWD becomes wider[136,137].

The study of the MWD of the polyarylates obtained from phenolphthalein and terephthalic acid chloride by gel permeation chromatography revealed a bimodal distribution with respect to the molecular weight, as shown in Fig. 10.[138]

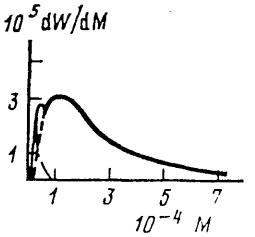


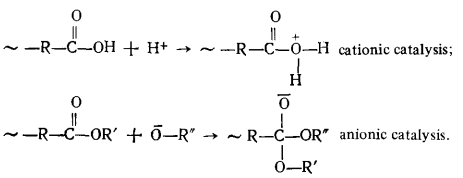
Figure 10. Molecular weight distribution curve for polyarylate.

This type of MWD can be explained by the fact that, together with the linear polyarylate, a cyclic polymer (macrorings) is formed[139]. The formation of cyclic polymers in the polycondensation reaction together with linear polymers had been observed earlier in the synthesis of polydimethylsiloxanes, poly(ethylene terephthalate), polyamides, and polyesters[140].

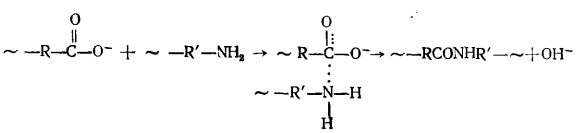
XII. CATALYSIS IN POLYCONDENSATION REACTIONS

Catalysis is known to play a major role in polycondensation processes[15,33,41,141,143]. The application of catalysts in polycondensation processes makes it possible to accelerate the reaction and to obtain polymers with a broad spectrum of properties[47,141,142,146,147].

Catalysis in non-equilibrium polycondensation reactions can proceed as cationic, anionic ionic-coordination, and free-radical process depending on the nature of the starting materials and the catalysts[15,141,142]. The intermediate complexes are illustrated schematically below:

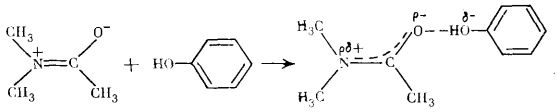


Accordingly, the mechanism of the polycondensation of a diamine with a dicarboxylic acid involving nucleophilic substitution is as follows[144]:

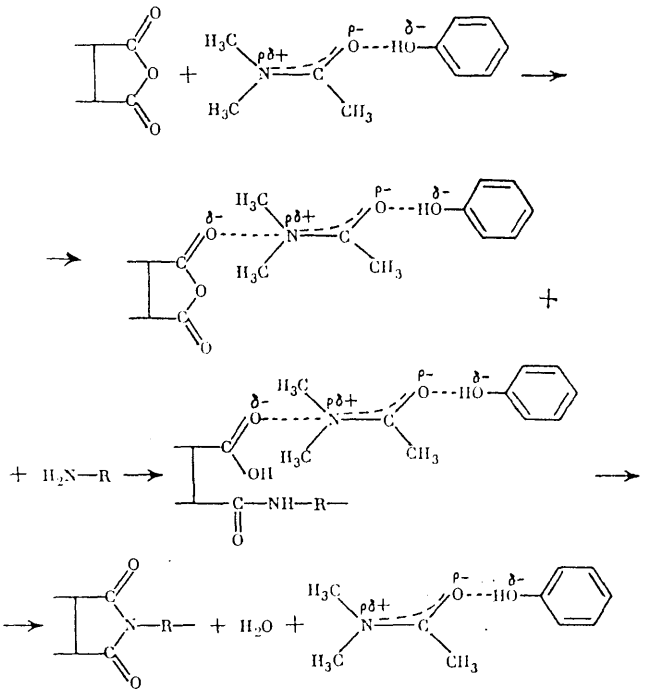


For the amide catalysis of the polyimide formation reaction, the following reaction mechanism, in which an amide–phenol

complex is formed initially, has been proposed[145]:

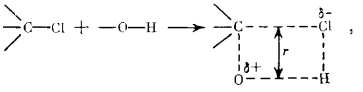


This is followed by the formation of a ternary catalytic complex:



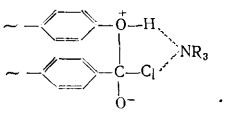
The imide ring is formed in this way and the complex is regenerated[145].

The following transition state has been proposed to account for the mechanism of the poly(ethylene terephthalate) formation reaction:



where r is the diameter of the "active component" of the activated complex[148].

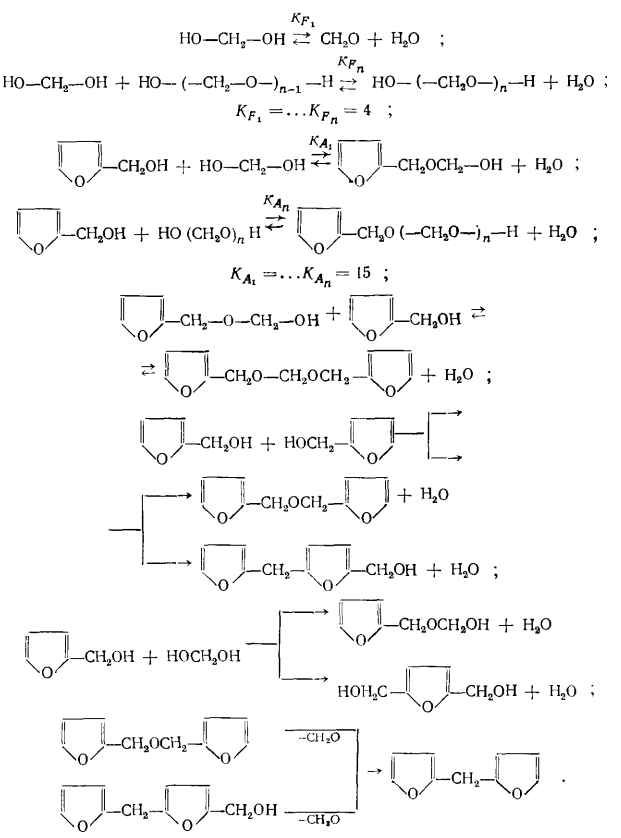
Ionic-coordination catalysis obtains, for example, in the presence of tertiary amines with formation of an intermediate complex, which probably has the following structure:



As will be shown below, the formation of such complexes facilitates the polycondensation process and makes it possible to obtain conformationally regular polymers.

Various compounds of many elements, indicated in Table 6, have now been investigated as polycondensation catalysts[15, 41, 129].

The following reaction scheme has been proposed for the condensation of furfuryl alcohol with formaldehyde in the presence of an acid catalyst (a 10% aqueous solution of 84% H_3PO_3):[149]

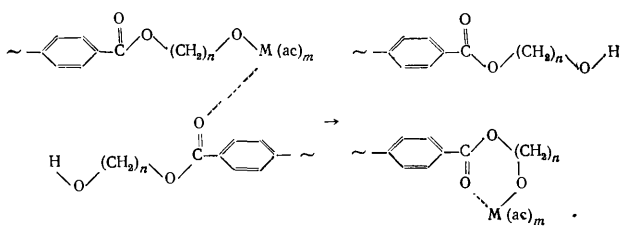


At the end of this reaction chain, difurfurylidenemethane becomes the main product.

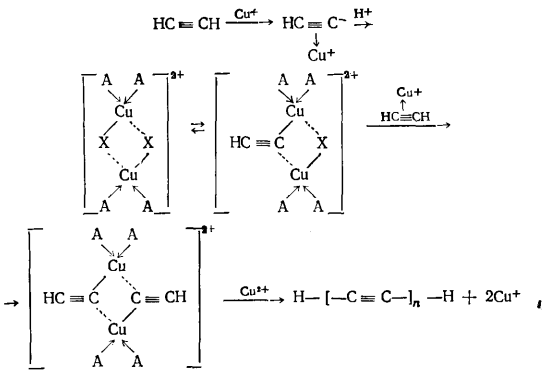
Table 6. Elements whose compounds have been used as polyesterification catalysts[15].

Period	Groups							
	I	II	III	IV	V	VI	VII	VIII
1	H							
2	Li	Be	B	C	N	O	—	— — —
3	Na	Mg	Al	Si	P	S	Cl	
	K	Ca	—	Ti	—	Cr	Mn	Fe Co Ni
4	Cu	Zn	—	Ge	As	—	—	
5	—	Sr	—	Zr	—	Mo	—	— — Pd
	Ag	Cd	—	Sn	Sb	—	—	
	—	Ba	La	—	Ta	—	—	Os Ir Pt
6	—	Hg	—	Pb	Bi	—	—	
7	—	—	—	Th	—	U	—	— — —

The effect of metal acetates as catalysts in the synthesis of poly(ethylene terephthalate) has been explained by the following scheme[147]:



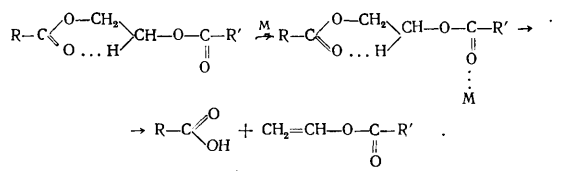
The free-radical catalysis by copper–amine complexes obtains, for example, in the oxidative polycondensation of acetylene, leading to the formation of carbyne—the third linear form of carbon[150]:



where A is the complexone residue.

The Andrianov reaction, which involves the catalytic polycondensation of organosilazanes, has been investigated on a large number of examples. Its general character has been demonstrated in relation to a series of organosilazanes and the formation of polycyclic polymers containing a trisilyl-substituted nitrogen atom in the chain has been established[151,152].

Together with the acceleration of the polycondensation, catalysts can also induce undesirable reactions involving the decomposition of the polymers, accompanied by the darkening of the products and the degradation of the macromolecules. The following mechanism of the action of metal ions as catalysts of the degradation of a polyester has been proposed[147]:



It is of interest to note that catalysts influence the reaction and the properties of polyheteroarylenes not only in the first but also in the second stage of reaction. This has been observed for polyimides obtained under the catalytic influence of phosphoric acid[153].

XIII. JOINT POLYCONDENSATION

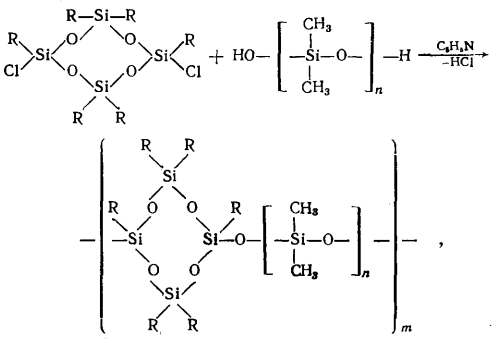
Joint polycondensation has been attracting increasing attention of investigators[103,109,154–160]. It has been established that anion-exchange resins can be used as effective catalysts in the joint polycondensation of dicarboxylic acid chlorides with bisphenols and glycols. The possibility of employing different types of anion exchangers and of obtaining copolymers with different microstructures arises under these conditions[161]. Studies of joint polycondensation have demonstrated the influence of the reactivity of the initial monomers and of the way in which the reaction is carried out on the structure of the polymer formed. Turska and co-workers derived a kinetic equation describing the joint polycondensation reaction of three bifunctional monomers A, B, and C. These monomers are selected in such a way that the monomer A reacts with the monomers B and C, but the latter do not react with one another[162]. The same workers studied the influence of the reactivity of the functional groups of the monomers on the composition of the copolymer and the structure of the macromolecular chain in the non-equilibrium polycondensation reaction[163] and determined the isokinetic temperature T_i for each pair of monomers for which the rate constants for both reactions are identical:

$$T_i = \frac{E_{AB} - E_{AC}}{R\,(B_{AB} - B_{AC})} ,$$

where E_{AB} and E_{AC} are the activation energies for the corresponding polycondensation reactions, B_{AB} and B_{AC} are the pre-exponential factors in the Arrhenius equation, and R is the gas constant.

If $K_{AB} > K_{AC}$ at a temperature below T_i, then at a temperature above T_i the relative reactivities of the monomers B and C are reversed and the latter becomes more reactive than the monomer B. Consequently the distribution of the B and C units along the macromolecular chain varies with temperature. On the other hand, at a reaction temperature equal to T_i a product of constant composition, independent of the degree of reaction and with a statistical distribution of the B and C units, is formed. Hence arises the possibility of regulating the joint polycondensation process by selecting an appropriate reaction temperature[156,163]. The joint polycondensation reaction can be directed, if so desired by the investigator, towards the formation of a statistical copolymer or a block copolymer. If, as usual, the two monomers are mixed with the intermonomer, then a statistical copolymer is always formed. On the other hand, if the intermonomer is gradually introduced into the mixture of the comonomers then a block copolymer is produced[154]. The slower the addition of the intermonomer, the more pronounced the block structure of the copolymer formed under these conditions[157].

An extremely interesting feature of polycondensation is the possibility of obtaining with its aid block copolymers having a polyblock structure, in contrast to polymerisation where block copolymers with only di- and tri-block structures are possible[110]. As an example, we quote Andrianov's synthesis[158] of block copolymers containing linear and cyclic groups, achieved by carrying out the reaction in pyridine:



where n = 2, 4, 12, 25, and 70.

The nature of the solvent in which the polyarylate is synthesised influences the structure of the copolymer obtained. The distribution of the units in the copolymer obtained by the reaction of isophthaloyl chloride with a mixture of di(4-aminophenyl) ether and di(4-aminophenyl) sulphone has been investigated as a function of the polycondensation conditions[159]. It was found that in sulpholan there is a distinct tendency towards the formation of blocks. However, in the presence of epoxypropane, which is a weaker acid acceptor, it is possible to obtain copolymers with a high content of alternating structures[159].

The order of mixing of the reactants is also extremely important. Thus, if a mixture of one diol and triethylamine is taken for the reaction after which the dicarboxylic acid chloride is added and only then the second diol is introduced, a block copolymer is obtained[109,160]. On the other hand, if triethylamine is added to a solution of the acid chloride and one diol and the second diol is only then introduced, a statistical copolymer is obtained[109].

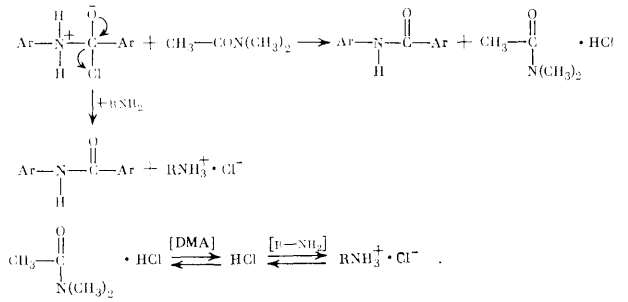
XIV. THE INFLUENCE OF SOLVENTS

The study of the mechanisms of the reactions used in non-equilibrium polycondensation has led to the discovery of the major role of solvents. This led in its turn to the discovery of conformationally specific polycondensation[25], of a method for the synthesis of block copolymers[154], etc.

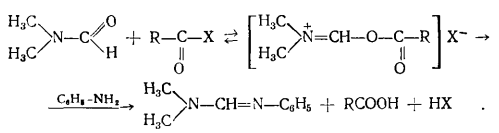
It has been shown that the nature of the solvent has a significant influence on the molecular weight and yield of the polymers formed in the non-equilibrium polycondensation of acid anhydrides and chlorides with aromatic diamines[164] and also in the reaction of phenol with formaldehyde and in other instances of polycondensation[165,166].

Sokolov found that the addition of water makes it possible to alter very appreciably the conditions in the synthesis of polyamides from dicarboxylic acid difluorides and dichlorides and diamines[156,167].

Herlinger et al.[168] showed that non-equilibrium polycondensation in solution in amide solvents proceeds via a stage involving the formation of a reaction complex of the acid chloride and the amine, which is followed by the formation of an amide linkage and the hydrochloride of dimethylacetamide:

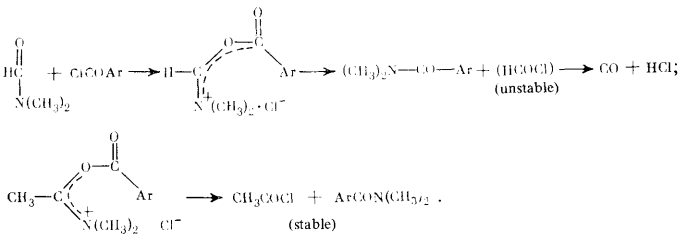


The study of the polycondensation of dicarboxylic acid halides with diamines in solution in dimethylformamide (DMF) showed that this too results in the formation of reactive adducts of the acid halides with DMF.[169] The later react with amines (for example, aniline) to form *N*,*N*-dimethyl-*N'*-phenylformamidine:

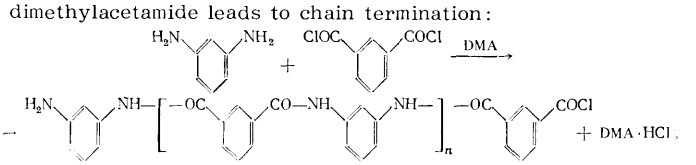


Under these conditions, the acid acceptor can also be the unreacted amine, which influences the course of the process, altering the ratio of the starting materials so that the course of the polycondensation reaction depends on the equilibrium $RNH_2.HCl \rightleftharpoons DMA.HCl$.[168]

In addition there is also the possibility of a transamidation reaction via the mechanism



This reaction, which has been studied using ^{14}C-labelled dimethylacetamide leads to chain termination:



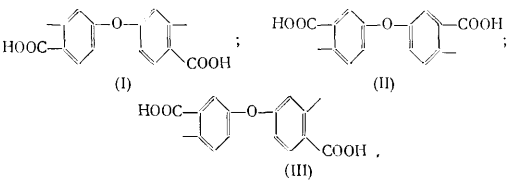
H_2N-polymer-$COCl + CH_3^{14}CON(CH_3)_2 \rightleftarrows H_2N$-polymer-$CO\text{-}N(CH_3)_2 + CH_3^{14}COCl$;

H_2N-polymer-$CON(CH_3)_2 + CH_3^{14}COCl \rightleftarrows CH_3\text{-}CO\text{-}NH$-polymer-$CO\text{-}N(CH_3)_2$.

The use of the tracer atom technique (^{14}C) showed that the rates of propagation and termination of the polymer chain are in the ratio 280 : 1. Kinetic studies demonstrated that 70 to 80 °C is the upper temperature limit beyond which a polymer with a high molecular weight can not be obtained owing to the high rate of the transamidation reaction and hence of chain termination[168].

An interesting case illustrating the role of the solvent is provided by the reaction of bis-α-diketones with tetramines, which is used for the synthesis of polyphenylquinoxalines[170]. It has been found that the rate of reaction of the amino- and keto-groups in chloroform is higher by a factor of 10^5–10^6 than in tetrahydrofuran.

The nature of the solvent in which the reaction takes place has a significant influence on the process. Thus all three isomeric structures are formed in the reaction of the anhydride of bis(3,4-dicarboxyphenyl) ether with 9,9-di(4-aminophenyl)fluorene[89]:

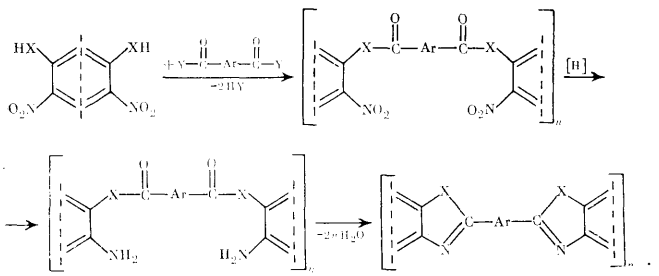


Their ratios vary somewhat depending on the nature of the solvent. Thus they are (I) : (II) : (III) = 0.33 : 0.18 : 0.49 in hexamethylphosphoramide and (I) : (II) : (III) = 0.46 : 0.11 : 0.43 in *N*-methylpyrrolidone. Steric factors and not the basicity of the amine play a significant role in this instance. It is of interest to note that the isomeric composition of the polyamidoacid in solution in *N*-methylpyrrolidone does not vary with time whereas in dimethyl sulphoxide there is a gradual enrichment in structure (I).

XV. NEW POLYMERS AND METHODS OF SYNTHESIS

We shall consider briefly certain examples characterising the advances in the creation of new polymers and the development of new methods of synthesis[171]. Great improvements

in the processes involving the synthesis of industrial polycondensation polymers (polycarbonates and carbamide and phenol-formaldehyde polymers) have been achieved recently[146,147]. Among the new synthetic processes, the reductive polyheterocyclisation reaction, constituting a new method of synthesis of polyheteroarylenes, has been described[172]. The synthetic reaction of polybenzazoles proceeds in accordance with the equation

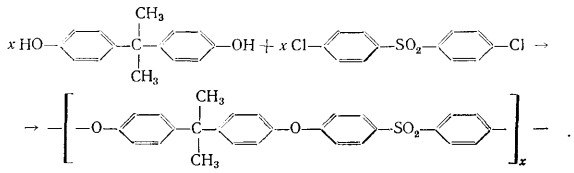


It is noteworthy that studies have been carried out recently whose aim was to seek new polycondensation methods. These include the work of Sokolov, who proposed two new methods for carrying out such reactions. These are the gas-phase polycondensation and emulsion polycondensation[173-176].

Emulsion polycondensation resembles closely interfacial polycondensation, since in both cases the reaction systems employed are heterogeneous. In emulsion polycondensation the reaction zone consists of the total volume of one of the phases and the rate-limiting stage is the chemical interaction[175,177]. The method of thin-layer interfacial polycondensation using monomeric aerosols has also been proposed[134,177].

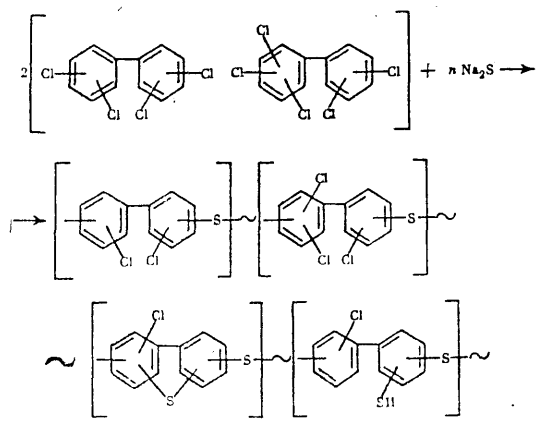
The solid-phase polycondensation used in the form of an improved modification as a method of synthesis of polyheteroarylenes should also be mentioned[178,179].

The dehydrochlorination of bisphenols and di(chlorophenyl) sulphone leads to the formation of polysulphonylethers[180,181]:



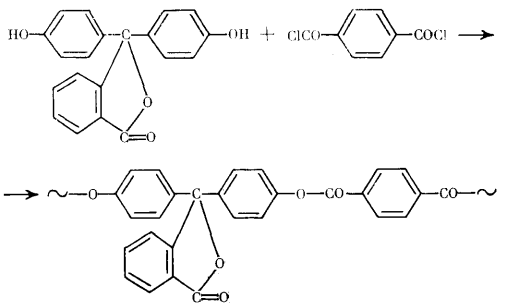
These polymers have a set of valuable properties and, in particular, they are imcombustible. The block copolymers based on oligosulphonylethers are especially interesting[182,183].

The polycondensation of polychlorobiphenyls with sodium sulphide leads to the formation of poly(biphenylene sulphides):



It is of interest that, although the functionality of the initial monomers is fairly high, soluble polymers are formed[184].

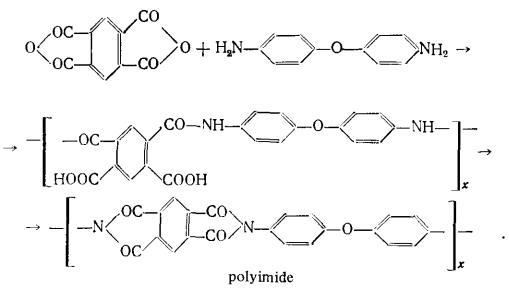
By carrying out the reaction of bisphenols with acid chlorides in the presence of tertiary amines, it is thus possible to obtain cardo-polymers[185]. The polyarylate formed in the reaction of terephthalic acid dichloride with phenolphthalein is an example of a cardo-polymer[185]:



A characteristic feature of cardo-polymers is that their chains contain carbon atoms incorporated simultaneously in cyclic groups making up the polymer chain (they are designated by circles below). Accordingly, the structure of the cardo-polymer can be represented schematically as follows:

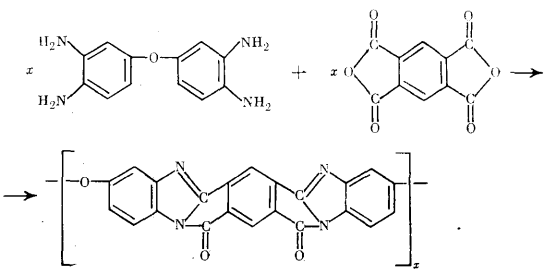


Polycyclisation comprises a large group of polycondensation reactions based on the interaction of dicarboxylic acid esters and fluorides as well as their other derivatives and tetracarboxylic acid anhydrides with diamines, hydroxyamines, mercaptoamines, and tetramines, leading to the formation of various polyheteroarylenes[37,59,63,64]. Thus polyamides, which are some of the most thermostable polymers, have been obtained by the reaction of diamines with acid dianhydrides[89,186-189]:



polyimide

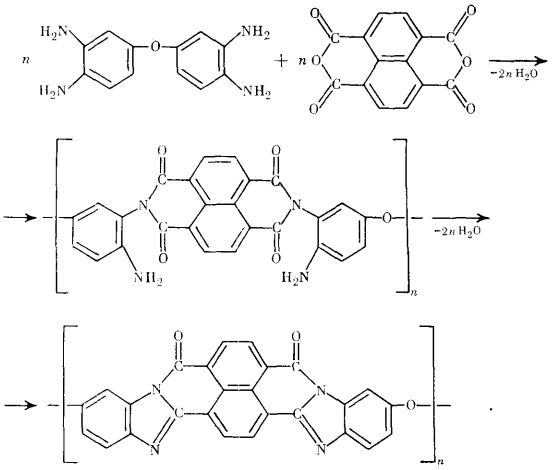
Ladder polymers, an example of which is provided by pyrrones, constitute an interesting group of thermostable polymers. The pyrrone formation reaction proceeds in accordance with the equation[37,60,190,191]



The synthesis of polyamidoacids, the corresponding polycarboximides, and pyrrones by the reaction of di(4-amino-3-carboxyphenyl)methane with the dianhydrides of pyromellitic

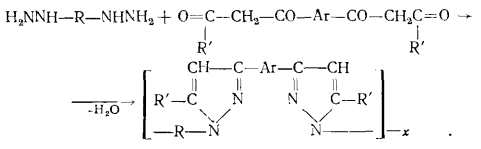
and benzophenone-3,3',4,4'-tetracarboxylic acids has been described[192].

The study of the reaction of di(3,4-diaminophenyl) ether with the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid showed that the heterocyclisation reaction proceeds via a stage involving the formation of aminoimide rings[193]:

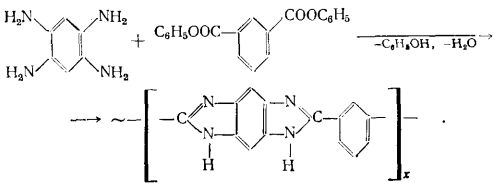


These are examples of a polycyclisation reaction which results in the formation of polymers containing various heterocycles. The great interest throughout the world in polymers of this kind can be explained by the fact that most of them are substances with high thermal stability and this feature has attracted much attention to them and has led to a very great increase in the efforts devoted to research in this field. During the last 10–15 years, when thermostable polymers have also attracted extensive interest, many hundreds if not thousands of polymers of this type have been obtained and it would be impracticable to describe the characteristics of all of them. One must quote several formation reactions of the most widely known polymers of this type in order to demonstrate their characteristic features.

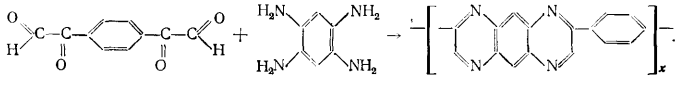
The formation reaction of polypyrazoles, where the starting materials are bis(β-diketones) and dihydrazides, proceeds in accordance with the equation[194]



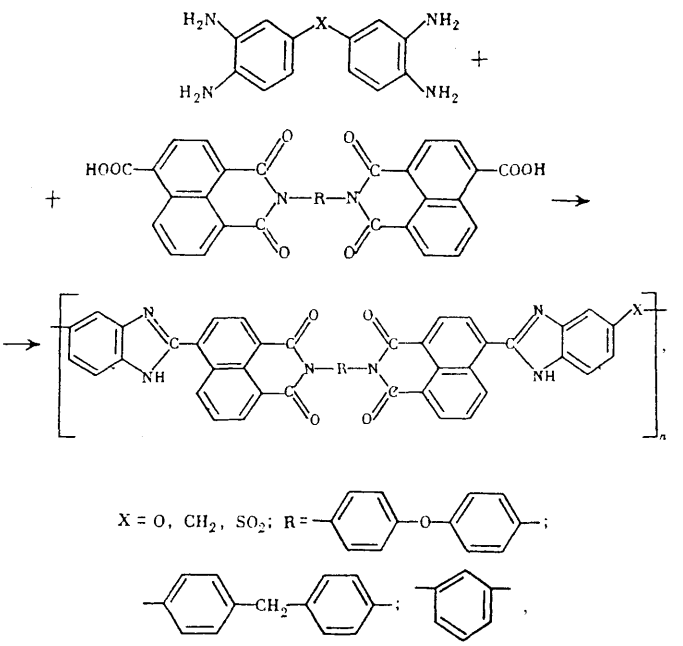
The formation reaction of polybenzimidazoles is[75,195]



Finally we may also mention the formation reaction of polyquinoxalines which involves the interaction of tetramines with dialdehydediketones or tetraketones[80,196]:



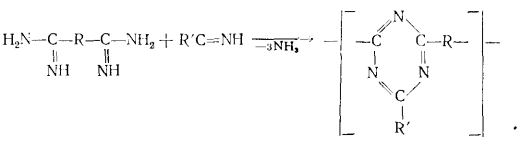
Polybenzimidazolimides, synthesised via the reaction[197]



constitute a new class of polymers. Many more reactions of this type could be quoted but those described above are sufficient to illustrate their general characteristics.

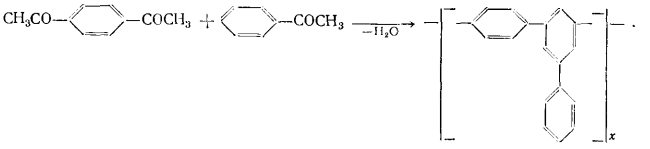
A few words should be devoted to a variety of the polycondensation reaction, namely the polycyclocondensation reaction. In contrast to the polycyclisation discussed above, where a polymer is formed initially and then a heterocycle, i.e. there is a two-stage process, the polycyclocondensation reaction proceeds in such a way that cyclisation is the first stage of the polymerisation process.

As an example, we may quote the formation reaction of triazine polymers involving the polycondensation of mono- and di-amidines[198]:



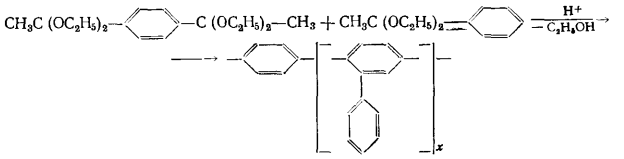
This reaction has attracted attention because the polymer obtained has rubber-like properties and a high thermal stability.

Another example is the recently discovered polycondensation reaction of ketones leading to the synthesis of polyphenylenes[199,200]:

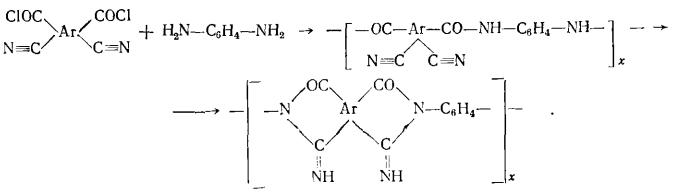


The polycondensation of acetyl groups involves the formation of a new benzene ring joined to the phenyl groups present in the initial monomer. This results in the formation of a soluble and fusible polymer. The reaction constitutes a new method of synthesis of thermostable polyphenylenes.

The reaction has been simplified by replacing the ketones by their ketals[201]. The polyphenylene formation reaction then proceeds in accordance with the equation



A novel instance of polycyclisation is isomerisation polycyclisation distinguished by the fact that the molecule of the initial monomer contains cyano-groups. As a result of this, low-molecular-weight products are not produced in the first stage of the reaction and instead there is addition to the triple bond with formation of a polyiminoimide[186]:



A series of polyheteroarylenes containing several heterocycles and carbocycles in the ring, for example, the imide and oxadiazole rings, the imide and benzimidazole rings, the imide and pyridine as well as pyrimidine rings in various combinations, etc. have been obtained[188,197,202].

An interesting group of dehydropolycondensation reactions is based on dehydrogenation with evolution of hydrogen[203]:

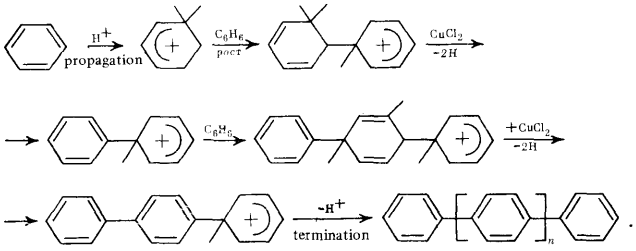
$$R_2BH + HBR_2 \rightarrow RB{-}BR + H_2 .$$

Oxidative dehydropolycondensation is a dehydrogenation reaction under the influence of oxidants and is widely used for the synthesis of various polymers.

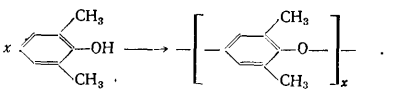
The oxidative dehydropolycondensation of acetylenic compounds is widely employed for the synthesis of polymeric structures containing triple bonds in the chain. A linear carbon polymer, namely carbyne, has been obtained by this reaction[204]:

$$n\,H{-}C{\equiv}C{-}H \rightarrow -(-C{\equiv}C-)_n- .$$

The benzene oxidation reaction, discovered by Kowacic and widely used by other investigators to synthesise polymeric structures, belongs to this class. In this case the oxidant is copper(I) chloride and the reaction thus involves the combination of residues with formation of a polyphenylene structure[205]:



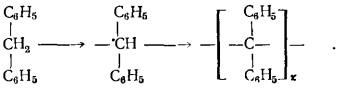
An interesting instance of the oxidative dehydropolycondensation reaction is the oxidation of 2,6-dimethylphenol, leading to the formation of poly(phenylene oxide), which is nowadays manufactured on an industrial scale[206]:



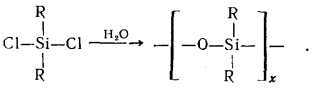
Finally we may mention the amine oxidation reaction used to obtain structures containing double bonds between nitrogen atoms as well as aromatic rings. The polymeric systems obtained in this way are of interest from various points of view[207]:

$$n\,(Ar)_2NH \rightarrow -[-Ar{-}N{=}N-]_n- .$$

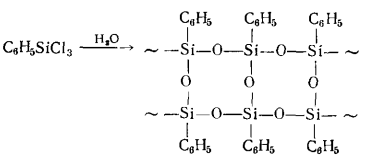
The polyrecombination reaction involves the synthesis of polymers in which the free radicals formed in the first stage from the peroxide abstract a hydrogen atom from the molecules of the initial monomer and thus give rise to free radicals which subsequently recombine to form a polymeric structure. In the case of diphenylmethane the reaction proceeds in accordance with the equation[22,208]



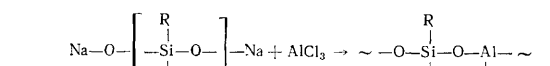
The syntheses of organoelemental polymers involving an increasing number of elements have developed very extensively. This field was initiated by the synthesis of polysiloxanes:



This reaction is used widely in industry to manufacture a wide variety of siloxane polymers and oligomers[11,209]. The use of trichlorophenylsilane as the starting material makes it possible to obtain ladder polymers of the type of polyphenylsiloxane[210,211]:



The reaction of organosiloxane blocks with metal salts leads to the formation of polyorganoaluminosiloxanes[212,213]:



The use of salts of other metals leads to the formation of polyorganometallosiloxanes[90,214].

A large number of organoelemental polymers have been obtained by the polycondensation reaction.

XVI. PROSPECTS FOR THE DEVELOPMENT OF POLYCONDENSATION

The present state of the study of polycondensation processes and their utilisation for the synthesis of polymers with a set of properties specified beforehand is characterised, as shown by the examples presented, by a series of significant achievements. There is no doubt that the further development of polycondensation synthesis will enrich polymer science in a large number of new polymers with a set of valuable properties[215]. The development of syntheses of various copolymers, among which mention may be made of

block copolymers of various types, which are of interest as starting materials for the preparation of separating membranes, is extremely promising. The synthesis of various kinds of polymers modelling natural polymers and biopolymers, particularly for use in medicine, is of great interest.

The problem of the study of the characteristic features of polycondensation is of great theoretical importance as regards control of the reactions involving the growth of the macromolecule in order to regulate the size and structure of the polymer chain. Control of the formation reaction of anomalous units, leading to the formation of heterounit polymers, is very important in this sense. This permits a more detailed regulation of the properties of the polymers obtained. The search for new reactions leading to the synthesis of polymers via polycondensation is one of the most important problems in this field. The expansion of the range of monomers and the wide variety of the structures produced are important in this instance.

It is now apparent that the development of new ways of carrying out the polycondensation reaction constitutes an important step towards advances in this field.

New possibilities for the regulation of the macromolecular structure are then created and one can synthesise the required polymers, in particular those with the required supermolecular structure, crystalline or amorphous, as well as conformationally regular polymers. Naturally problems associated with the synthesis of new polymers satisfying the needs of the modern technology and various branches of industry as regards new materials superior to those already known remain important. Among the important problems of this kind, one may point to those involving the formation of thermostable polymers, polymers with a high mechanical strength, effective adhesive properties, hardness, and elasticity, incombustible polymers, polymers with a set of specific properties of the kind possessed by semi-conductors, photosensitive polymers, etc.

In the field of polycondensation processes themselves, there is every reason to expect new advances in the immediate future involving the achievement of controlled polycondensation synthetic methods. Among problems of this kind, one may point to those involving the regulation of the molecular weight in order to obtain high-molecular-weight polymers and also the search for new polycondensation processes. A most important task is to achieve control of synthetic processes of a kind which would permit the regulation of the geometrical and heterounit structures of polymers and hence the synthesis of polymers with the required optimum set of properties. One of the most important ways of solving problems of this kind involves the wide-scale development of research into catalytic processes in polycondensation, the discovery of new ways of regulating the processes involving the synthesis of polymers in polycondensation reactions, and the expansion of the assortment of such reactions.

In conclusion one should note that, as can be seen from the examples presented, there has been considerable progress in the field of polycondensation. New synthetic reactions of polymers are being discovered and synthetic reactions already known are being investigated and improved. As a result, science is being enriched in a large number of new polymers and many of the polymers already known, now obtained by improved methods, have acquired a set of more valuable properties. Our time is characterised by a deepening of the knowledge of increasingly complex chemical reactions and the formation of new extremely complicated polymeric structures, which reflects the growing sophistication of the chemical art in the synthesis of polymers. Methods for the formation of anomalous units, leading to a heterounit structure of polymers, which is an important factor in the determination of the relation between the structure and properties of polymers, have been devised. Finally, an especially characteristic feature of the polycondensation synthesis is the synthesis of polymers not only for constructional purposes but also to an increasing extent of compounds with specific properties such as thermostable, semiconducting, electrically conducting, photoelectrically active, and biologically active polymers, biopolymers, catalysts, ion-exchange resins, and similar polymers with specific properties.

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Nesmeyanov Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 252525 U.D.C. 541.64:547.315.2

Organometallic Catalysis in Diene and Cyclo-olefin Polymerisation Processes. I. The Polymerisation and Copolymerisation of Dienes Under the Influence of Organometallic Transition Metal Compounds. The Stereoregulation Mechanism

B.A.Dolgoplosk and E.I.Tinyakova

The results of experimental studies on the synthesis of individual organometallic transition metal compounds and of studies on their catalytic activity in stereospecific diene polymerisation and copolymerisation processes are surveyed. The kinetics of the polymerisation under the influence of various nickel-, chromium-, titanium-, and molybdenum-containing systems are examined. The stereoregulation mechanism and the principal characteristics of coordination copolymerisation are discussed on the basis of the experimental data.
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I. INTRODUCTION

The question of the nature of the active centres affecting various types of stereoregulation and of the mechanism of their action has been at the centre of the attention of investigators from the instant of the establishment of the field of synthesis of rubbers by the polymerisation of dienes. This is mainly due to the fact that the properties of the polymers are directly related to the structure of the units in the polymer chain. Thus polybutadiene containing only 1,2-units has a glass point $t_g = -10$ °C, while the rubbers made from it are brittle already at 0 °C. *cis*-Polybutadiene is a highly elastic rubber with $t_g = -108$ °C, while *trans*-polybutadiene is a crystalline fibre with a melting point of ~+140 °C. In the polymerisation of isoprene the number of different variants of the microstructures of the units increases and new structures associated with the inhomogeneity of the distribution of 1,4-units in terms of the "head to tail" and "head to head" arrangements (1,4–1,4; 1,4–4,1; 4,1–1,4) appear. This also applies to other dienes.

Highly stereoregular butadiene and isoprene polymers of different structures were first obtained in the presence of Ziegler type catalysts consisting of transition metal compounds and organoaluminium compounds. Other components ensuring a higher selectivity of the action of the catalytic system and reproducibility of the results are added to them in in many instances.

Table 1 presents the compositions of systems characterised by the highest stereospecificity; some of them are of industrial importance. It is seen from the results presented that only lanthanide-containing systems are equally stereospecific for the formation of *cis*-units in the polymerisation of both butadiene and isoprene. The cobalt and nickel systems are stereospecific for butadiene and lead to the formation of a polyisoprene with a mixed structure. The $TiCl_4$–AlR_3 system is a stereospecific catalyst of the *cis*-polymerisation of isoprene, while in the polymerisation of butadiene many *trans*-units are formed. Vanadium systems based on $VCl_3(VOCl_3, VCl_4)$ are stereospecific in the formation of *trans*-units in the polymerisation of butadiene, while systems without a halogen cause the formation of 1,2(3,4)-units.

Table 1. Catalytic systems with stereospecific activity in the polymerisation of dienes.

Catalytic system*	Contents of units, %				Refs.
	cis-	*trans*-	1,2-	3,4-	
Butadiene					
$TiI_4 + AlR_3$ (Al/Ti = 4÷8)	95	2	3		[1–4]
$TiI_2Cl_2 + AlR_3$ (Al/Ti = 4÷8)	90	—	—		[5]
$TiCl_4 + AlR_3$	57—71	27—41	2		[6, 7]
$CoCl_2 \cdot H_2O + R_2AlCl$ (Co : Al : H_2O = = 1 : 150 : 10)	92	5	3		[2, 8]
Ni(naphth)$_2$ + R_2AlCl	92	5	3		[8]
$LnX_3.D + R_3Al$ (Al/Ln = 20)	98	1.5	0.5		[9, 10]
$Ln(OCOR)_3 + R_2AlCl + R_3Al$**	97	2	1		[9, 10]
$VCl_3(VCl_4, VOCl_3) + R_3Al$	0	97—99	1—3		[12, 13]
$Rh(acac)_3 + R_2AlCl$	—	98	—		[14, 15]
$V(acac)_3 + R_3Al$	9—11	3—12	78—86		[16]
$Cr(acac)_3 + R_3Al$	1—2	1—10	88—99		[17, 18]
$MoO_2(OR)_2 + R_3Al$	—	—	98		[2]
$Ti(OR)_4 + R_3Al$	—	—	88—98	—	[19, 20]
Isoprene					
$TiCl_4 + AlR_3$ (Al/Ti = 1.2)	94—96	0	3—4	3	[7, 21]
$CoX_2 + R_2AlCl + 10H_2O$	up to 70	15—22	1—3	up to 31	[22, 23]
$LnX_3.D + R_3Al$ (Al/Ln = 20)	94—98	0	2—6	0	[10, 11]
$Ln(OCOR)_3 + R_2AlC + R_3Al$ **	94—95	0	5	0	[10, 11]
$VCl_3(VCl_4, VOCl_3) + R_3Al$	0	80—99	0	9	[12, 13]
$Ti(OR)_3[Ti(OR)_4] + R_3Al$	0	—	—	94—99	[19, 20]

*Ln = Nd, Pr, Ce, or La; D = complex-forming agent.
**$Ln(OCOR)_3$: R_2AlCl : R_3Al = 1 : 2–3 : 20.

An enormous number of studies have been made on the kinetics of the polymerisation of dienes and olefins under the influence of Ziegler systems. The experimental data, particularly the effective activation energies and the reaction orders with respect to the catalyst and the monomer, cannot be used to characterise the active centres, since the probability of the formation of new active centres based on more reduced compounds of the metal increases with increase of temperature or with increase of the concentration of the system components.

The authors of the early investigations assumed that the organoaluminium compound plays the main role in chain propagation steps. However, as research into this field developed, it became clear that the main role in the chain propagation steps is played by the transition metal compound. The concept of the two-centre (multicentre) stereoregulation mechanism in which the atoms of both the transition metal and aluminium are involved has become most widely adopted. The complexity of the composition of Ziegler-Natta catalytic systems and the wide variety of the reactions between their components precluded the finding of direct experimental approaches to the elucidation of the nature of the active centres and the stereoregulation mechanism. New possibilities for the solution of this problem have arisen as a result of the employment of individual organometallic compounds for the initiation of polymerisation.

II. THE SYNTHESIS OF ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS AND THE STUDY OF THE STEREOSPECIFICITY OF THEIR ACTION IN THE POLYMERISATION OF DIENES

The organic derivatives of transition metals with carbon–transition metal π-allyl and σ-bonds which have been synthesised and used in the polymerisation of dienes are listed in Table 2. Compounds having the general formula $\pi\text{-}R_nM$, where R = allyl, crotyl, or pentenyl and M = Ni^{2+}, Co^{3+}, Cr^{3+}, Cr^{2+}, V^{3+}, Nb^{3+}, or Rh^{3+}, were obtained from the corresponding alkenylmagnesium halides and metal chlorides in diethyl ether. Their stability increases in the sequence allyl < crotyl < pentenyl. We have shown[29,39,41] that the pentenyl complexes of many transition metals are stable at 0–20 °C, while the corresponding π-allyl complexes are stable below −20 °C.[24]

π-Alkenylnickel halides have been largely obtained by the Fischer method from nickel carbonyl and the corresponding alkenyl halide.

π-Oligodienylnickel chloride has been obtained by a new method of synthesis based on the interaction of nickel chloride and AlR_3 in the presence of small amounts of a diene (molar ratios Ni : Al : diene = 1 : 3–5 : 10–30),[26] for example:

$$NiCl_2 + R_3Al \rightarrow R_2AlCl + RNiCl \xrightarrow{C_4H_6} R(C_4H_6)_nNiCl.$$

At the end of the reaction the hydrocarbon solution was washed with an aqueous solution of acid to remove completely the organoaluminium compound. The π-alkenylnickel chloride remained entirely in the hydrocarbon solution, the yield amounting to ~90% of theoretical. The oligodienylnickel chloride is more stable than $\pi\text{-}C_3H_5NiCl$ and $\pi\text{-}C_4H_7\text{.NiCl}$. The π-allyl compounds π-RNiOY have been obtained from $\pi\text{-}R_2Ni$ and the corresponding acid (CCl_3COOH, $CH_3C_6H_4OSO_2H$, and o,o-dinitrophenol).[27]

Tribenzyltitanium and tris(trimethylsilylmethyl)titanium can be obtained from $TiCl_3$ and the corresponding organolithium compounds at temperatures in the range −30° to −40 °C in 50–60% yield[37]. However, TiR_3 and other transition metal compounds can be synthesised more conveniently in a more reduced state by a method which we proposed[36] on the basis of the reaction

$$MR_{n+1} + LiC_2H_5 \rightarrow LiR + MR_nC_2H_5 \rightarrow MR_n + 0.5C_2H_4 + 0.5C_2H_6 \quad ,$$

where R = benzyl, trimethylsilylmethyl, or allyl. The reaction is carried out in a hydrocarbon solvent and the yield of MR_n is nearly quantitative. Trimethylbenzyltitanium is fairly stable at 20 °C in solution in aromatic and aliphatic hydrocarbons; the presence of even small amounts of an electron donor [tetrahydrofuran (THF), ether] reduces sharply the stability of the compound. In hydrocarbon solutions tribenzyltitanium is associated and the concentration of paramagnetic species is only 2–3% of the total content of Ti^{3+}, in contrast to tri-π-allyltitanium, which is monomeric in solution and the concentration of the paramagnetic species corresponds to that of Ti^{3+}.[52] Benzyltitanium halides are stable only below −30 °C, disproportionating quantitatively on raising the temperature with formation of equivalent amounts of titanium(II) and titanium(IV) compounds[37]. The occurrence of this reaction precludes the synthesis of TiR_3 from $TiCl_3$ + RMgCl(RLi) above −20 °C.[53] The disproportionation reaction is fully suppressed in the presence of small amounts of diene[51]. It has been shown that butadiene is inserted in the Ti–benzyl bond with formation of trioligodienyltitanium. A similar compound has also been obtained by the reaction of $TiCl_3$ with oligodienyl-lithium in solution in toluene[52]. Tri-π-oligodienyltitanium is monomeric in solution and the concentration of paramagnetic species corresponds to that of Ti^{3+} determined by reaction with Fe^{3+}; the compound is stable for a long time at room temperature[52].

Table 2. The organometallic compounds synthesised and used as catalysts of the polymerisation of dienes.

Organometallic compound	Methods and conditions of synthesis	Refs
$\pi\text{-}R_2Ni$(R = allyl or crotyl)	$NiCl_2$ + RMgCl; ether; −30–−40°	[24]
π-RNiX (R = allyl, crotyl, pentenyl, or cyclohexadienyl; X = Cl, Br, or I	$Ni(CO)_4$ + RCl; benzene; 60–65°	[25]
$\pi\text{-RNiCl}$ [$R = R'(diene)_n$]	$NiCl_2 + AlR_3' + C_4H_6(C_5H_8)$ (1 : 2÷5 : : 10÷30); 0°	[26]
π-RNiOY (R = allyl or crotyl)	$\pi\text{-}R_2Ni$ + HOY; toluene; −30°; OY = CCl_3COO, CF_3COO, o,o-dinitrophenoxy, or $CH_3C_6H_4OSO_2$	[27]
$\pi\text{-}R_3Cr$ (R = allyl, pentenyl, or crotyl)	$CrCl_3$ + RMgX; ether; −20°	[28, 29]
$\pi\text{-}R_2Cr$ (R = allyl or pentenyl)	$CrCl_2$ + RMgX; ether; 0-20°	[29]
$\pi\text{-}R_2CrOSi\vert SiO_2$	$\pi\text{-}R_3Cr + HOSi\vert SiO_2$	[30]
$\pi\text{-}RCr(OSi)_2\vert SiO_2$	$\pi\text{-}R_3Cr + HOSi\vert SiO_2$	
$\pi\text{-}RCr(OAl\vert)_2\vert Al_2O_3$	$\pi\text{-}R_3Cr + HOAl\vert Al_2O_3$	[30]
$\pi\text{-}R_2CrCl$	$\pi\text{-}R_3Cr$ + HCl; toluene; −30°	[31]
$(C_6H_5CH_2)_4Ti$	$TiCl_4$ + RMgCl; ether + heptane; −25°	[32, 33]
$(C_6H_5CH_2)_3TiI$	$TiR_4 + I_2$; toluene + benzene; −20°	[33]
$(C_6H_5CH_2)_3TiBr$	$TiR_4 + Br_2$; toluene + benzene; −20°	[33]
$(C_6H_5CH_2)_3TiCl$	TiR_4 + HCl; toluene; −16°	[33]
$[(CH_3)_3SiCH_2]_nTiCl_{4-n}$	$TiR_4 + TiCl_4$	[34, 35]
$(C_6H_5CH_2)_3Ti$	$(C_6H_5CH_2)_4Ti + LiC_2H_5 \rightarrow [(C_6H_5CH_2)_3TiC_2H_5] \rightarrow TiR_3$	[36]
$(C_6H_5CH_2)_2TiI$	$TiR_3 + 0.5I_2$; toluene + benzene; −35°	[37]
$(C_6H_5CH_2)_2TiCl$	TiR_3 + HCl; toluene + benzene; −35°	[37]
$C_6H_5CH_2TiCl_2$	TiR_3 + 2HCl; toluene + benzene; −20–−35°	[37]
$C_6H_5CH_2TiI_2$	$TiR_3 + I_2$; toluene + benzene; −35°	[37]
$[(CH_3)_3SiCH_2]_3Ti$	$TiCl_3 + LiCH_2Si(CH_3)_3$; ether; −50°	[37]
$(C_3H_5)_3Ti$, $(C_4H_7)_3Ti$	$TiCl_3$ + RMgX; ether; −30°	[1, 38]
$(C_5H_9)_3Ti$	$TiCl_3$ ($TiCl_4$) + RMgX; ether	[39]
$[C_3H_5(C_4H_6)_n]_3Ti$ ($n = 2 \div 10$)	$TiR_3 + (2-10)C_4H_6$; toluene; −20°	[40]
$(C_5H_9)_3V$	$VCl_4 + C_5H_9MgX$; ether; −30°	[41]
$[(CH_3)_3SiCH_2]_3V$	$VCl_3 + (CH_3)_3SiCH_2Li$; ether + heptane	[42]
$(\pi\text{-}C_3H_5)_4Mo$(W, Zr)	$MCl_4 + C_3H_5MgX$	[43,45]
$(C_3H_5)_nMo$(W, Zr)X_{4-n}	$M(C_3H_5)_4 + HX$	[46]
$(C_3H_5)_3Nb$	$NbCl_3 + C_3H_5MgX$; ether	[47]
$(C_3H_5)_2NbCl$	$NbR_3 + HCl$	[47]
$(C_3H_5)_3Rh$	$RhCl_3 + C_3H_5MgCl$	[47]
$(C_6H_5CH_2)_3Nd$	$NdCl_3 + LiCH_2C_6H_5$; ether; −25°	[48]
$RLnCl_2$(R = $C_6H_5CH_2$, $(C_6H_5)_3C$)	Ln + RCl; THF; 20–40°	[49, 50]

Tribenzylneodymium is stable only below −20 °C, but in the presence of dienes it is stabilised and induces their polymerisation at 50 °C. All three Nd–benzyl bonds are involved in the polymerisation process and the active centre is a trioligodienyl derivative of neodymium, which proved to be fairly stable[48].

Thus it has been established in relation to Ti^{3+}, Nd^{3+}, and other ions that the oligodienyl derivatives of transition metals are much more stable than the corresponding π-allyl, benzyl, etc. derivatives. This finding has been explained[52] on the basis of the idea of the stabilising action of the π-complexes of the transition metal with the double bonds of the oligodienyl chain.

Arylalkyl-lanthanide dichlorides have been obtained by the oxidative addition of arylalkyl halides to the metallic lanthanide (Nd, Pr, Ho, or Gd) in THF.[49,50] A distinctive feature of the compounds formed is their ability to metallate THF.

The reaction involving the addition of dienes and olefins to the M–H bond is a source of the formation of organometallic compounds. Thus the interaction of dienes with nickel, cobalt, and chromium hydrides leads to the formation of the corresponding π-allyl complexes, which can participate in polymerisation like the compounds described above[54]. In essence, this type of reaction obtains in systems of the Ziegler type when hydrogen is used to regulate the molecular weight:

$$pMX_n + H_2 \rightarrow pH + HMX_n \xrightarrow{C_4H_6} \pi\text{-}C_4H_7MX_n \xrightarrow{C_4H_6} \text{chain propagation},$$

where p is the polymer chain.

An effective system for the polymerisation of dienes is formed under the influence of nickel and other metal subhalides obtained by heating *in vacuo*.[55] In this case a very small amount of paramagnetic NiCl species, incorporated in the mass of nickel chloride, is produced. These species become organometallic active centres initiating the polymerisation of butadiene, particularly after the extinction of the paramagnetic signal by hydrogen (the formation of $HNiCl|NiCl_2$). In a number of instances metal hydrides can serve as a convenient source in which active centres are formed. In view of the lower stability of σ bonds compared with π-allyl bonds in olefins (styrene and ethylene), the reaction of the latter usually terminates with formation of oligomers and the active centre propagating the chain in HNiX:[56]

$$HNiX + H_2C{=}CHC_6H_5 \rightarrow H_3C{-}CH(C_6H_5)NiX \xrightarrow{H_2C=CHC_6H_5}$$
$$\rightarrow H_3C{-}CH(C_6H_5)CH_2{-}CH(C_6H_5)NiX \rightarrow H_3C{-}CH(C_6H_5)CH{=}CHC_6H_5 + HNiX\ .$$

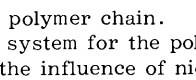
Studies have established that organometallic compounds of transition metals are the true active centres for the polymerisation of dienes and the stereospecificity of their action is determined by the nature of the metal and the ligands surrounding it.

Table 3 presents experimental data characterising the stereospecificity of the action of various organometallic compounds in the polymerisation of butadiene and isoprene. Polymerisation proceeds in all cases throughout the addition of the monomer to the carbon–transition metal bond. The active centre of the growing chain is an organometallic compound of the alkenyl type with a π-allyl or σ bond depending on the nature of the transition metal. π-Allylnickel halides are *trans*-regulating catalysts leading to the formation of crystalline *trans*-polybutadiene and *trans*-polyisoprene[57–59,65]. π-Allylnickel iodide is the most active in the π-allylnickel halides. One should note that the π-alkenylnickel halides are as a rule dimeric and the order of the polymerisation reaction with respect to the catalyst is 0.5.[57] It follows from this that only small numbers of monomeric forms, which exist in equilibrium with the associated species, participate in the polymerisation reaction.

It is seen in relation to $\pi\text{-RNiOCOCCl}_3$ as an example that the substitution of the halogen by a more electronegative group reverses the stereospecificity of the action of the catalyst (from *trans*- to *cis*-). The most effective and stereospecific, in relation to *cis*-stereoregulation in the polymerisation of butadiene, are the products of the interaction of π-RNiX with electron acceptors (A_1 and A_2); charge-transfer complexes (CTC) and complexes with the transfer of an anion (ATC):

$$\underset{\vdots\ A_1^-}{\pi\text{-}R\overset{+}{N}iCl} \qquad \underset{ATC}{\pi\text{-}R\overset{+}{N}i\,[ClA_2]^-}$$
CTC

Table 3. The stereospecificity of the action of organometallic compounds of transition metals in the polymerisation reactions of butadiene and isoprene.

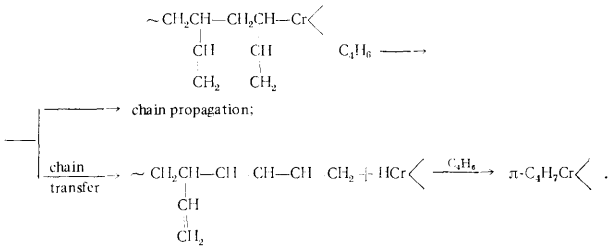
Organometallic compound	Contents of units, %				Refs.
	cis-	*trans*-	1,2-	3,4-	
Butadiene					
π-RNiX (X=Br, I)	0	95	5		[57–59]
$\pi\text{-RNiOCOCCl}_3$	92–95	3–6	2		[27]
	93.5	4.5	2		[27]
$\pi\text{-RNiOSO}_2C_6H_4CH_3$	48	45.5	3.5		[27]
π-RNiX·A* (X=Cl, Br, I)	90–97	2–5	1–3		[60, 61]
π-R_3Cr (R = allyl, crotyl, or pentenyl)	0	20	80		[31]
$\pi\text{-R}_2\text{CrOC}_4\text{H}_9$	12	14	74		[62]
$\pi\text{-RCr(OC}_2\text{H}_5)_2$	6	19	75		[62]
π-R_2CrOSi|SiO_2 (aluminosilicate)	0	92–97	3–8		[30]
$\pi\text{-RCr(OAl)}_2|\text{Al}_2\text{O}_3$	86	9	5		[62]
$\pi\text{-R}_2\text{CrOCOCCl}_3$	93	4	3		[31]
π-R_2Cr + HCl (1 : 2)	90	5.5	4.5		[31]
$(C_6H_5CH_2)_4Ti$	20	20	60		[33]
$(C_6H_5CH_2)_3TiCl$	35	19	48		[63]
$(C_6H_5CH_2)_3TiBr$	66	13	21		[63]
$(C_6H_5CH_2)_3TiI$	97	1	2		[63]
$(C_6H_5CH_2)_3Ti$	22	18	60		[40, 64]
$(C_6H_5CH_2)TiCl$	54	8	38		[40, 64]
$(C_6H_5CH_2)_2TiI$	91	7	2		[40, 64]
$C_6H_5CH_2TiCl_2$	0	90	10		[40, 64]
$C_6H_5CH_2TiI_2$	32	55	13		[40, 64]
$(C_3H_5)_4Nb$	0	0	100		[47]
$(C_3H_5)_2NbCl$	91	5.5	3.5		[47]
$(C_3H_5)_3Rh$	0	94	6		[47]
$(C_3H_5)_2RhCl$	0	93	7		[47]
$(C_3H_5)_3MoOCOCCl_3$	0	2	98		[44, 46]
$(C_3H_5)_3MoCl$	2	11	87		[44, 46]
$(C_3H_5)_3MoI$	0	2	98		[44, 46]
$(C_3H_5)_3WCl$	0	8	92		[45]
$(C_3H_5)_3WOCOCCl_3$	0	13.5	86.5		[45]
$(\pi\text{-}C_3H_5)_4Zr$	55	7	38		[45]
$(C_6H_5CH_2)_3Nd$	0	95	5		[48]
Isoprene					
π-RNiI	0	95	0	5	[65]
π-RNiX·A*	23–55	27–66	1–2	10–20	[66]
π-R_3Cr	17.5	18	28.5	36	[30]
π-R_2Cr	0	0	47.5	52.5	[29]
$\pi\text{-R}_2\text{CrOSi}|\text{SiO}_2$	0	97	0	3	[62]
$\pi\text{-R}_2\text{CrOC}_4\text{H}_9$	25	22	29	22	[62]
$\pi\text{-R}_2\text{Cr(OAl)}_2|\text{Al}_2\text{O}_3$	95	0	0	5	[62]
$(C_6H_5CH_2)_4Ti$	0	75	7	18	[67]
$(C_6H_5CH_2)_3TiCl$	19	36	6	39	[67]
$(C_6H_5CH_2)_3TiBr$	69	0	4	27	[67]
$(C_6H_5CH_2)_3TiI$	87	0	0	13	[67]
$(C_6H_5CH_2)_3Nd$	0	95	0	5	[48]

*A = acceptor—chloranil, chloral, CCl_3COOH, CCl_3COCl, $M(OCOCCl_3)_2$ (M = Zn, Ni, or Mg), $TiCl_4$, AlX_3, $NiCl_2$, $CoCl_2$, etc.

Chloranil, fluoranil, chloral, trichloroacetic acid, etc. have been investigated as the acceptors A_1 and various metal salts playing the role of Lewis acids ($AlCl_3$, zinc trichloroacetate,

$ZnCl_2$, $NiCl_2$, and other salts) have been studied as the acceptors A_2.[60,61,68–70] In both cases (CTC and ATC) the increase of the efficiency of the action of the system is associated with the increase of the positive charge on the nickel atom. Some of the catalytic systems investigated proved to be extremely effective even at −15 °C. Investigations have established that, when π-RNiX interacts with acceptors, side reactions take place and lead to the decomposition of a considerable proportion of the organonickel compound, as a result of which the amount of the effective active centres propagating the polymerisation reaction is 10–15% of the π-RNiX introduced[71–73]. In all cases the reaction is of first order with respect to the catalyst.

Organochromium compounds (π-R_3Cr and π-R_2Cr) lead preferentially to the formation of 1,2(3,4)-units in the polymerisation of dienes[29,31]. In all cases low-molecular-weight polymers are formed (the average degree of polymerisation is 25–30) containing a conjugated system of double bonds at one end of the chain. The molecular weight of the polymer is independent of the monomer concentration although the propagation reactions have been shown to be of first order with respect to the monomer[31]. Hence it follows that not only the propagation reaction but also the chain transfer reaction proceeds with participation of the monomer:



The quantitative Diels–Alder reaction of polymer chains with maleic anhydride indicates the *trans*-conformation of the diene end of the chain (analogue of *trans*-piperylene). The use of π-allyl compounds of chromium thus leads to the possibility of obtaining oligomeric unsaturated products with the functional group at one end of the chain.

In contrast to the comparatively unstable π-alkenyl derivatives of chromium, the organometallic compounds of chromium(II) and chromium(III), bound chemically to the SiO_2 or aluminosilicate surface, are fairly stable, propagating the polymerisation process via the "live" chain mechanism even at ~70 °C. These systems are extremely stereospecific for the formation of *trans*-units in the polymerisation of various dienes[30,62]. The *trans*-conformation of the units is fully retained in the copolymerisation of dienes. The above systems can be used to obtain the corresponding crystalline homopolymers (butadiene and isoprene) as well as amorphous *trans*-copolymers. All the groups bound to the chromium atom participate in the polymerisation reaction and the molecular weight of the polymer increases continuously with the degree of polymerisation. The similarity of the copolymerisation constants (r_1 and r_2) for butadiene, isoprene, and piperylene must be noted. The identity of the microstructures of the polymers and the identify of the constants of the copolymerisation of butadiene with isoprene permitted the conclusion that the chromium oxide catalyst known previously (CrO_3 on a carrier) acts via analogous stages involving organochromium compounds[30].

π-Alkenylchromium compounds, bound chemically in Al_2O_3, are *cis*-stereoregulating catalysts in the polymerisation of butadiene and isoprene, in contrast to the compounds described above. However, they rapidly lose their activity at a comparatively low degree of polymerisation[62]. The most important distinctive feature of this system is the formation of a polymer with a very high molecular weight even at a low degree of conversion, which indicates a very high rate of chain propagation. When the allyl groups in π-R_3Cr are substituted by electronegative groups, the system becomes *cis*-stereoregulating[31].

Like polyallylchromium compounds, tetrabenzyltitanium induces the formation of mainly 1,2(3,4)-units. The substitution of one benzyl group by a chlorine, bromine, or iodine atom increases the content of *cis*-units (in the sequence indicated). Tribenzyltitanium iodide is a highly stereospecific catalyst for the synthesis of *cis*-polybutadiene. The somewhat smaller content of *cis*-units in the polyisoprene formed can be due to the contamination of the system by a very small amount of oxygen-containing impurities. It has been established that the addition of small amounts of THF or diethyl ether to $(C_6H_5CH_2)_3TiI$ reverses the stereospecificity of the action of the system from 1,4-*cis*-specificity to 1,2-stereoregulation, as in the case of organolithium compounds. Only one benzyl group participates in polymerisation steps under the influence of $(C_6H_5CH_2)_4Ti$ and $(C_6H_5CH_2)_3TiI$; this is illustrated by the data in Fig. 1, which presents the yields of toluene in the decomposition of the polymerisation mixture by an aqueous solution of acid at the end of the polymerisation reaction[33],

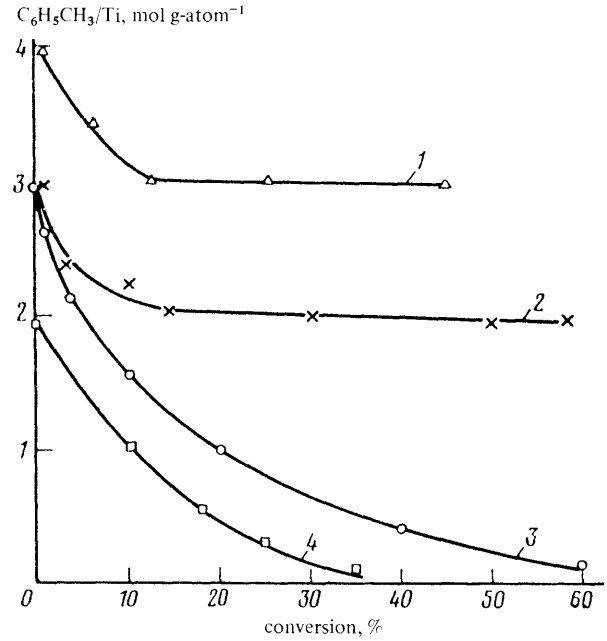


Figure 1. The consumption of benzyl groups in the polymerisation of butadiene {$[C_4H_6]$ = 5 M} under the influence of benzyl derivatives of titanium(IV) and titanium(III):[33,37,40]
1) $(C_6H_5CH_2)_4Ti$, [Ti] = 5 × 10^{-3} M, 50 °C, *o*-xylene;
2) $(C_6H_5CH_2)_3TiI$, [Ti] = 1.5 × 10^{-3} M, 25 °C, *o*-xylene;
3) $(C_6H_5CH_2)_3Ti$, [Ti] = 10 × 10^{-3} M, 50 °C, toluene;
4) $(C_6H_5CH_2)_2TiI$, [Ti] = 3 × 10^{-3} M, 25 °C, toluene.

It is important to note that tetrabenzyltitanium remains in the quadrivalent state throughout the polymerisation process. Titanium(III) compounds have so far been investigated only

in the polymerisation of butadiene. Tribenzyltitanium leads to the preferential formation of 1,2-units and, in contrast to tetrabenzyltitanium, all the benzyl groups are involved in the polymerisation reaction (Fig. 1). Among all the halogeno-derivatives of tervalent titanium, only $(C_6H_5CH_2)_3TiI$ is a highly effective catalyst of the synthesis of *cis*-polybutadiene. The polymerisation proceeds with an appreciable induction period due to the slow initiation stage—the insertion of butadiene in the titanium–benzyl bond. The induction period disappears completely following the addition of organoaluminium compounds (R_3Al and R_2AlCl; Al/Ti = 1 mol mol^{-1}) to R_2TiI. It has been shown for the $(C_6H_5CH_2)_2$. .TiI + R_2AlCl system[74] that the exchange reaction results in the immediate substitution of the benzyl groups by isobutyl groups, to which butadiene adds in a broad front:

$$(C_6H_5CH_2)_2TiI + (iso\text{-}C_4H_9)_2AlCl \rightarrow (iso\text{-}C_4H_9)_2TiI + (C_6H_5CH_2)_2AlCl .$$

At the end of the polymerisation process, after the decomposition of reaction mixture with an aqueous solution of acid, all the benzyl groups of the initial dibenzyltitanium iodide can be detected quantitatively in the form of toluene (Fig. 1).[74] It follows from the results that the true active centre in the Ziegler "titanium" system used under industrial conditions to synthesise *cis*-polybutadiene is apparently the compound R_2TiI.

Tri-π-allylniobium leads to the formation of amorphous 1,2-polybutadiene and the substitution of even only one of its allyl groups by chlorine leads to *cis*-stereoregulation. Among all the polyallyl derivatives of transition metals, only the rhodium compounds lead to *trans*- and not 1,2(3,4)-units.[47]

Tetra-allyl derivatives of molybdenum and tungsten do not themselves induce the polymerisation of dienes; polymerisation catalysts based on them are formed after the substitution of one allyl group by a halogen atom or other anionic species[43,45,46]. Two allyl groups in the resulting active centres are linked to the Mo(W) atom by a π-allyl bond and are not involved in polymerisation; one allyl group is linked to the metal by a σ bond and polymerisation proceeds via the latter. The organometallic active centres indicated are extremely stereospecific for the formation of amorphous and crystalline 1,2-polybutadiene. The syndiotactic arrangement of units predominates in the chain[44].

Like $(\pi\text{-}C_3H_5)_3Rh$, tribenzylneodymium leads to *trans*-structures in the polymerisation of butadiene and isoprene[48].

Triphenylmethylneodymium dichloride, containing 3–4 THF molecules in the coordination sphere, becomes an effective *cis*-regulating catalyst of the dimerisation of isoprene and butadiene after the introduction of tri-isobutylaluminium (Al/Nd = 3–5 mol mol^{-}).[49] The role of AlR_3 is still obscure—it is not clear whether it is involved only in complex formation with THF or whether it plays the role of an electron acceptor, forming complexes with $R'NdCl_2$. One cannot rule out the possibility that, as in the $(C_6H_5CH_2)_2TiI$ + R_2AlCl system examined above, the rate-limiting stage in this instance is the addition of the first diene molecule to the Nd–C bond, while the organoaluminium compound eliminates the induction period by replacing the triphenylmethyl group by the isobutyl group in the $(C_6H_5)_3CNdCl_2$ molecule.

The *trans*-isomer and not the *cis*-isomer is involved in the polymerisation of piperylene under the influence of transition metal compounds and RLi in hydrocarbon media in the vast majority of cases. This is correlated with the fact that *trans*-piperylene is capable of bidentate coordination to the metal. For the same reason, only the *trans*-isomer enters into the Diels–Alder reaction with maleic anhydride.

The polymerisation of cyclohexadiene can lead to two types of structure with the *cis*-conformation of units:



1,4-unit 1,2-unit

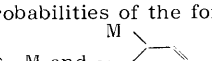
An amorphous polymer with approximately equal contents of the 1,4- and 1,2-units is formed under the influence of RLi in hydrocarbon and solvating media and systems of the Ziegler type (R_3Al + $TiCl_4$, R_3Al + VCl_3, etc.). The equal contents of the 1,4- and 1,2-units are apparently correlated with the equal probabilities of the formation of the active centres  -M and . Blocks of 1,2-units cannot arise in the chain owing to steric hindrance. A crystalline polymer with a melting point of the crystalline phase of ~270 °C is formed under the influence of complexes of π-allylnickel halides with electron acceptors (chloral etc.). The polymer contains more than 90% of 1,4-units and its glass point is ~120 °C.[75]

Table 4. Kinetics of the polymerisation of dienes under the influence of organometallic compounds of transition metals.

Catalytic system	Solvent	Reaction order w.r.t. monomer	Reaction order w.r.t. catalyst	E_a^{eff}, kcal mol^{-1}	Refs.
	Butadiene				
$(\pi\text{-RNiI})_2$	benzene	1	0.5	15.5	[57]
π-RNiI; [Ni] = 1·10^{-3}—1·10^{-5}	benzene		1		[76]
$(\pi\text{-}C_4H_7NiCl)_2\cdot 2Ni(OCOCCl_3)_2$	toluene	1	1	6.4	[77]
$(\pi\text{-}C_5H_9NiCl)_2\cdot 2Ni(OCOCCl_3)_2$	toluene, chlorobenzene	1.4—1.6	1	10	[78]
$(\pi\text{-}C_5H_9NiCl)_2\cdot 2Zn(OCOCCl_3)_2$	toluene, hexane	1.6—1.35	1	10	[78]
$(\pi\text{-}C_4H_7NiCl)_2$.chloranil	toluene	1	1	6.2	[79]
$(\pi\text{-}C_4H_7NiCl)_2\cdot 2CCl_3COOH$	toluene	2	1	12.1	[80]
$(\pi\text{-}C_5H_5NiCl)_2TiCl_4$	heptane	0—1*	1	14.6	[81]
π-RNiOCOCCl$_3$	toluene	1.5	1	11	[27]
π-R$_3$Cr	toluene	0	2	19	[31]
R$_3$TiI	toluene	1	0.5	8	[33]
R$_4$Mo+C$_3$H$_5$I	toluene	0	1	12	[46]
R$_4$Mo+CCl$_3$COOH	toluene	1	1	13	[47]
	Isoprene				
π-RNiI	toluene	0—1*	0.6	19	[65]
π-RNiOCOCF$_3$	toluene	1	1	19	[82]
π-R$_3$Cr	toluene	0—1*	1	17	[29]
π-R$_2$CrOSi|SiO$_2$	toluene	1	1	10	[30]

*At low monomer concentrations the rate of polymerisation increases with increasing concentration, while at higher concentrations (2–4 M and above) the rate is independent of the monomer concentration. The lower the catalyst concentration[29,65] and temperature[81], the lower the monomer concentration at which the zero order of the reaction with respect to the monomer is observed.

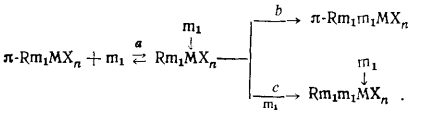
III. KINETICS OF THE POLYMERISATION OF DIENES UNDER THE INFLUENCE OF ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS

The kinetics of the polymerisation of butadiene and isoprene, in particular the reaction orders with respect to the monomer and the catalyst and the effective activation energy have been studied for a series of systems characterised by different stereospecificities of their action. In certain cases the concentration of the effective active centres for the

chain transfer reaction were determined experimentally. The results of these investigations are summarised in Table 4.

The effective activation energies E_a^{eff} for various systems vary from 6 to 19 kcal mol^{-1}. The π-RNiCl.chloranil, π-RNiCl.Ni$(OCOCCl_3)_2$, and tribenzyltitanium iodide systems are characterised by very low activation energies (6 to 8 kcal mol^{-1}). In most cases the rate of polymerisation of dienes is proportional to the concentration of the organometallic compound. In polymerisation under the influence of di-π-allylnickel iodide the order of the reaction at the catalyst concentration normally employed, i.e. $[Ni] > 10^{-3}$ M, is 0.5–0.6. Hence it follows that, like the initial π-allylnickel iodide, oligodienylnickel iodides exist in a dimeric form and the polymerisation reaction involves the monomeric form π-RNiI. The reaction order of 0.6 for the polymerisation of isoprene indicates a somewhat greater tendency of oligoisoprenylnickel iodide towards dissociation. At very low π-RNiI concentrations (10^{-5}–10^{-6} M) the reaction is first order with respect to the catalyst in the polymerisation of butadiene[76], which suggests that at such concentrations the monomeric form π-RNiI predominates.

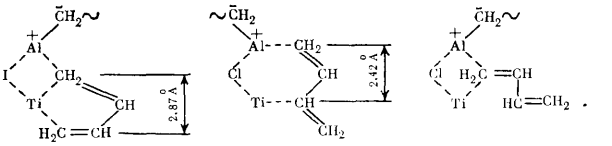
The order of reaction with respect to the monomer varies from 1 to 2, which reflects the influence of the stage in which the monomer is coordinated to the active centre. The mechanism of the incorporation of the monomer into the polymer chain presupposes an equilibrium stage involving the coordination of the monomer to the active centre and the stage in which it is inserted in the chain via a unimolecular or bimolecular mechanism:



Pathway *b* presupposes a unimolecular mechanism of the insertion of the coordinated monomer in the polymer chain via the C–M bond, while pathway *c* presupposes a bimolecular mechanism involving the displacement of a coordinated monomer by another monomer molecule (from the solution). There is a possibility that both reaction pathways operate simultaneously and the order with respect to the monomer can vary from 1 to 2 depending on which of the above stages limits the overall rate of the process.

IV. THE MECHANISM OF STEREOREGULATION IN THE COORDINATION POLYMERISATION OF DIENES

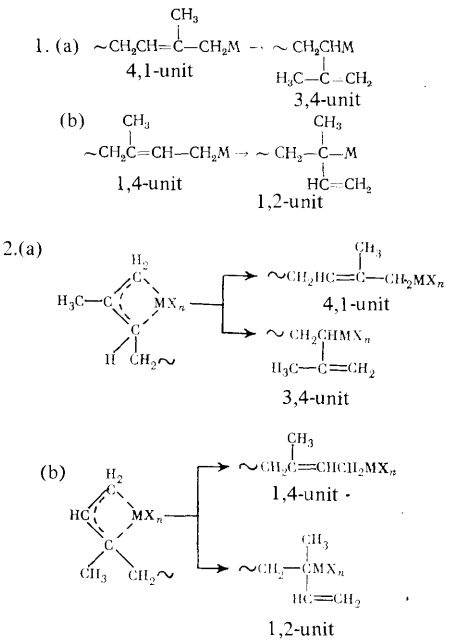
In the majority of studies on the polymerisation of dienes under the influence of Ziegler systems published previously the nature of the active centres and the polymerisation mechanisms were regarded from the same standpoint as in the consideration of the polymerisation of olefins. The structure of a bimetallic complex with bridge bonds was attributed to the active centre. In the first investigations it was assumed that chain propagation proceeds via the C–Al bond of the organoaluminium compound bound in a complex with a transition metal salt. Later schemes presuppose that the transition metal plays a decisive role in this complex and that the monomer is inserted not only in the Al–C bond but also in the carbon–transition metal bond. Furukawa[83] assumed that the structure of the units formed is determined by the length of the C–M bond which is correlated with the electronegativity of the metal. With decrease of the distance between two neighbouring sites, the structure becomes more favourable for coordination in the sequence *cis*-addition, *trans*-addition, and 1,2-addition, in which suitable distances are 2.87, 2.42, and less than 2.42 Å respectively:



In Ziegler catalysis stereoregulation is achieved by a complex catalyst having two coordination centres. The idea that a second, non-transition metal (aluminium) etc. must be present in the complex proved invalid after the possibility of the stereospecific catalysis under the influence of individual organometallic compounds of transition metals had been established. The first stage of the polymerisation reaction is coordination of the monomer to the transition metal.

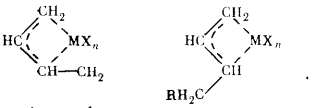
1. The Mechanism of the Formation of 1,4-*cis*- and *trans*-Units

In considering the question of the stereoregulation mechanism, we begin with the assumption that the structure of the units formed on polymerisation is determined by the structure of the terminal unit in the active centre and not the configuration of the monomer in solution[84–86]. This means that the *cis*- and *trans*-units are not genetically linked to the cisoid or transoid state of the monomer. The microstructure of the polymer chain already yields some information about the nature of the active centres. Thus in the organometallic σ-compounds of transition metals and lithium and in the π-allyl complexes the contents of 1,2- and 3,4-units also reflect a definite conformation of the active centre, for example:



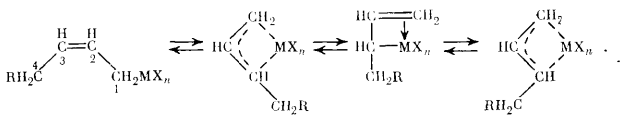
The formation of 1,2- and 3,4-units is genetically linked to a specific concentration of the terminal σ- or π-allyl active centre. The simultaneous presence of 1,2- and 3,4-units in polyisoprene therefore indicates the inhomogeneity of the chain structure in terms of the "head to tail" arrangement (the 1,4–1,4, 1,4–4,1, and 4,1–1,4 structures).

Examples of organometallic σ-compounds of transition metals initiating polymerisation are provided by titanium(IV) compounds as well as the organomolybdenum compounds R
|
π-R_2MoX, in which only the allyl group linked to molybdenum by a σ bond participates in chain propagation. The organometallic derivatives of alkali and alkaline earth metals and apparently the majority of organolanthanide compounds belong to a similar type. The alkenyl derivatives of transition metals, particularly those containing the metal in a reduced state, are formed as the stable compounds of the π-allyl type with two possible configurations (*anti*- and *syn*-), for example, for the crotyl derivatives, we have

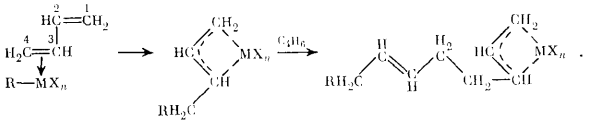


anti-complex *syn*-complex

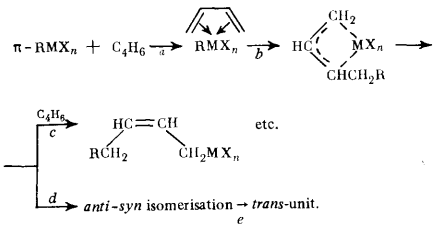
The *anti*-complex can be regarded as a seed giving rise to a *cis*-unit, while the *syn*-complex is a similar seed for a *trans*-unit. Tolman established for the first time that, when butadiene adds to HNi^+L_4 (L = phosphate ligand), an *anti*-complex is formed initially and isomerises subsequently to the *syn*-complex[87]. The *anti–syn* isomerisation can be represented only as a process proceeding via an intermediate σ-state, in which the metal is bound to a third carbon atom, because direct *cis–trans* transitions are energetically difficult:



The isomerisation takes place as a result of the migration of the "counterion" in the allyl conjugation system. The equilibrium amount of the σ-forms in the π-allyl complexes depends on the nature of the metal and the surrounding ligand. Naturally the electron-donating compounds forming complexes with the transition metal, which include also the monomer undergoing polymerisation, displace the equilibrium towards the σ-forms. If there is one vacancy (for coordination) at the transition metal, the diene can be coordinated via only one double bond, assuming a transoid conformation in the coordination sphere of the metal. The primary insertion of the monomer in the chain can then lead to a *trans*-unit:[85]

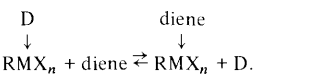


However, in the vast majority of cases the conjugated diene plays the role of a bidentate ligand, which assumes a cisoid conformation on the metal. This entails the transition from the π-allyl structure of the active centre to the σ-state:



The bidentate coordination of the conjugated diene is most likely for the monomeric form of the organometallic compound, characterised by the greatest number of vacancies for coordination.

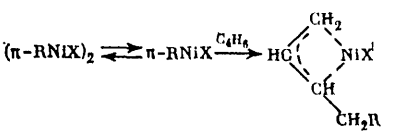
The polymerisation reaction consists of a sequence of stages involving the formation of a π-complex with the diene and its conversion into a π-alkenyl complex after the insertion of the diene in the chain with subsequent transition to the σ-state on coordination with the next monomer molecule (reactions *a–c*). Pathway *d* leads to the *anti–syn* isomerisation of the complex and the formation of *trans*-units. Thus, in polymerisation under the influence of monomeric forms of the organometallic compound, the chain microstructure is determined by the ratio of the rates of growth and isomerisation of the active centre. For systems in which the reaction is of first order with respect to the monomer, one may expect that, at very low monomer concentrations where the "lifetime" of the terminal unit increases, the number of *trans*-units should increase at the expense of the *cis*-units. This has been confirmed experimentally in the case where individual organonickel and Ziegler systems with participation of titanium and cobalt compounds were used[88] (Fig. 2). The results of studies presented in Fig. 2 show that in all cases indicated an appreciable decrease of the content of the *cis*-units and the corresponding increase of the content of *trans*-units are observed at low monomer concentrations (up to 0.4 M). Any factors favouring the "sticking" of the terminal unit in the active centre increase the role of the isomerisation in reaction. Electron-donating compounds (D) (ethers, sulphides, and amines) have a similar effect, being coordinated to the transition metal and displacing the diene:

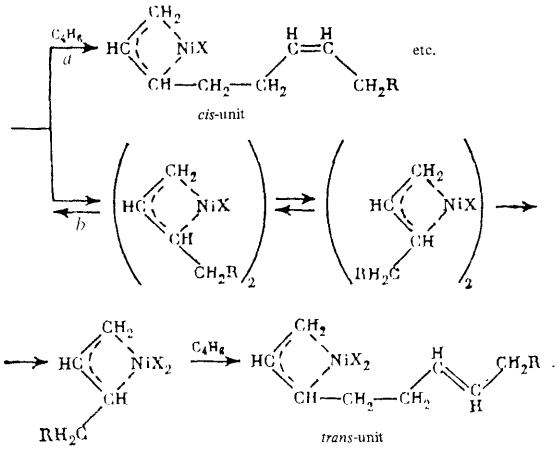


As will be shown below, the second monomer (m_2) has an analogous effect in copolymerisation if the rate of its insertion in the chain is less than the rate of insertion of the first monomer (m_1).

The question of the stereoregulation mechanism in cases where the organometallic active centre is in an associated state and the main true active centre in the chain propagation stage is the monomeric form is of great interest. This applies, for example, to the *trans*-regulating π-alkenylnickel halides, which exist in solution in the form of dimers and for which the reaction order with respect to the catalyst is 0.5,[57] and also to the butadienyl and isoprenyl derivatives of lithium. The latter exist in a hydrocarbon solution in the form of the associated species $(RLi)_4$ and the reaction order with respect to the catalyst is 0.25.[91,93] It follows from the data presented that, in the instances indicated, generally a small number of the monomeric active centres, in equilibrium with the associated species, participate in the polymerisation.

The mechanism of the chain propagation reaction involving π-alkenylnickel halides is[86,89]





In the primary product of the addition of the diene to the monomeric form π-RNiX the unit has the *cis*-conformation. In the associated species formed subsequently the π-alkenyl unit undergoes the *anti–syn* (*cis–trans*) isomerisation, which leads to *trans*-units on subsequent dissociation[89]. Since the fraction of the monomeric forms is very small, the associated species, not involved in the chain propagation steps, play a decisive role in the formation of microstructures. It is essential to note that only *trans*-β-butene is formed in the hydrogenolysis of π-crotylnickel chloride with complete absence of *cis*-butene[90]. This shows that the equilibrium concentration of the *syn*-form of π-crotylnickel halides is close to 100%.

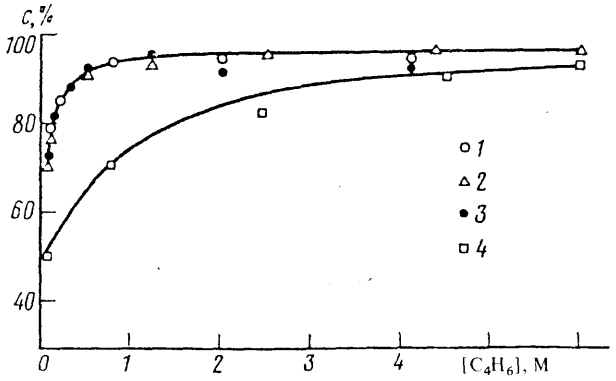
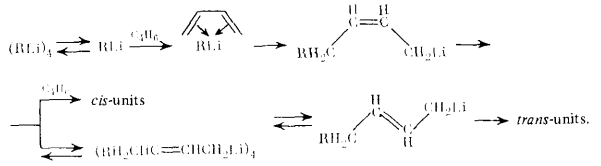


Figure 2. The influence of the monomer concentration on the microstructure of polybutadiene[88] (*c* = content of *cis*-units): *1*) π-C_5H_9NiCl–$Ni(OCOCCl_3)_2$; *2*) π-$C_3H_5NiOCOCF_3$; 3) $CoCl_2$–R_2AlCl; 4) TiI_2Cl_2–R_3Al; *1*), 3), and 4) 20 °C; 2) 40 °C; *1*), 3), and 4) solvent–toluene; *2*) solvent–heptane.

In the case of organolithium compounds the chain microstructure depends greatly on the RLi concentration in solution, which is illustrated by the data in Table 5. With decrease of the RLi concentration, the content of the *cis*-units in polyisoprene and polybutadiene increases. Presumably at vanishingly low concentrations of organolithium compounds only the *cis*-units are formed. The higher content of the *cis*-units in polyisoprene compared with polybutadiene for the same RLi concentration is consistent with the higher rate of chain propagation. It has been shown[93] that the rate of homopolymerisation of isoprene is significantly higher than that of butadiene. The mechanism of stereoregulation in the polymerisation of dienes under the influence of organolithium compounds must be represented by the same general scheme as for π-allylnickel halides:



The *cis–trans* isomerisation in the associated species apparently proceeds as a result of the transfer of the counterion (Li^+) to neighbouring molecules in the associated species and not via a unimolecular mechanism, because direct *cis–trans* transitions require a high activation energy.

Table 5. The influence of the catalyst concentration on the microstructure of the polymers obtained under the influence of organolithium compounds (20 °C, solvent—heptane).

[RLi], M	Contents of units, %				Refs.	[RLi], M	Contents of units, %				Refs.
	1,4-*cis*	1,4-*trans*	1,2-	3,4-			1,4-*cis*	1,4-*trans*	1,2-	3,4-	
	Butadiene						Isoprene				
0.073	30	46	24	—	[91]	0.061	74	18	0	8	[91]
0.0124	44	46	10	—	[91]	0.001	78	17	0	5	[91]
0.0003	47	45	8	—	[91]	0.0001	84	11	0	5	[91]
0.000054	70	28	2	—	[91]	0.000008	97	0	0	3	[91]
0.00001	86	10	4	—	[92]						

Polyakov et al.[94] showed for the first time that polymerisation on crystalline ethyl-lithium with supply of the diene from the gas phase takes place very slowly and leads to the preferential formation of 1,2(3,4)- and *trans*-units. Such a structure is characteristic of polymerisation involving the more polarised C–Li bond in the associated species.

The structure of such associated species depends greatly on their composition, which is indicated by the different compositions of the butenes formed on decomposition of the homoassociated crotyl-lithium species or mixed associated species incorporating crotyl-lithium and lithium alkyl by water or acid. In the former case β-butenes are formed preferentially, while in the latter α-butene is the preferred product[95].

The differences between the microstructures of polyisoprene and polybutadiene at the same RLi concentration can also be explained by the different rates of the *cis–trans* isomerisation in the associated species.

It was shown above that, depending on the nature of the ligands, either *trans*- or *cis*-units are formed in the presence of the same transition metal. It might have been expected that the rate of propagation in a *cis*-regulating system (v_a) would be significantly higher than in a *trans*-regulating system (v_b). Table 6 presents data illustrating the decrease of the rate of chain propagation (v_a/v_b) in the

presence of the same metal (Ni, Cr, and Ti) when the stereospecificity of the catalytic action is reversed from *cis*-stereoregulating to *trans*-stereoregulating.

Table 6. Comparison of the rates of chain propagation in the *cis*- and *trans*-stereoregulating systems[96].

No.	Catalytic system	Contents of units, %				v_a/v_b
		cis-	*trans*-	1,2-	3,4-	
	Isoprene					
1a	π-RCr(OAl)(OAl) | Al_2O_3	95	0	0	5	10^3
1b	R(R)Cr—O—Si | SiO_2	0	95	0	5	
	Butadiene					
2a	π-RNiCl·Ni(OCOCCl$_3$)$_2$	97	0	3		$7.8\cdot10^2$
2b	(π-RNiI)$_2$	0	95	5		
3a	$(C_6H_5CH_2)_3TiI$	95	2	3		$7.4\cdot10^3$
3b	$(C_6H_5CH_2)_4Ti$	20	20	60		

The positive role of electron-accepting components forming complexes with the organometallic active centre consists in a decrease of the probability of the formation of the associated species and in an increase of the rate of chain propagation. It is noteworthy that mainly *trans*-structures (95–98% of *trans*-units) are produced in systems involving vanadium compounds characterised by very high rates of chain propagation (indicated by the formation of isoprene and butadiene polymers with very high molecular weights). When account is taken of the considerations described above concerning the stereoregulation mechanism, this can be due by the very high rate of the *cis*–*trans* isomerisation or monodentate coordination of the diene.

2. The Mechanism of the Formation of 1,2(3,4)-Structures

The preferential formation of 1,2(3,4)-units in the polymerisation of dienes under the influence of RLi in solvating media or under the influence of RK(RNa) is always associated with an increase of the polarity of the C–M bond. As in all the anionic systems, leading to the preferential formation of 1,2(3,4)-structures, in the copolymerisation of butadiene (m_1) with styrene (m_2) in systems of this kind, styrene is much more reactive than butadiene ($r_2 \gg r_1$). On the other hand, in coordination systems dienes are appreciably more reactive than styrene regardless of the nature of the stereoregulation, which is illustrated by the data in Table 7.

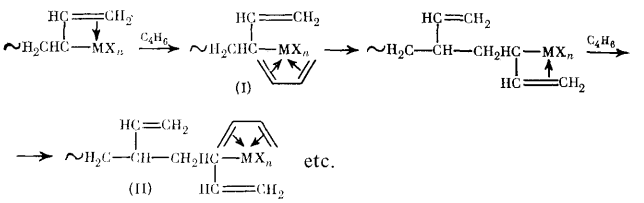
The results presented show that the formation of 1,2(3,4)-units in the systems considered is associated with the coordination mechanism of the catalytic action and not with the polarisation of the C–M bond. As mentioned above, the preferential formation of 1,2(3,4)-units is characteristic of organometallic compounds of the type MR_n ($M = Ti^{3+}$, Ti^{4+}, Cr^{3+}, or Cr^{2+}), R_3MoX, R_3WX, etc. and the formation of a crystalline or amorphous polymer with a syndiotactic arrangement of units (for R_3MoX and R_3WX) is characteristic of the polymerisation of butadiene. Many of the systems indicated in Table 7 are also active in olefin polymerisation processes, which indicates the stability of the organometallic σ-compounds. The stability of the C–M σ-bond increases in the polymerisation of dienes as a result of its conjugation with the double bond.

Table 7. The relative reactivities of butadiene (m_1) and styrene (m_2) in coordination copolymerisation (solvent—toluene).

Catalytic system	Contents of units in butadiene chain component, %			r_1	r_2	Refs.
	cis-	*trans*-	1,2-			
RLi*	0	9	91	0.2	8.0	[97]
RLi**	43	50	7	10	0.035	[98]
$(C_3H_5)_3MoOCOCCl_3$	8	2	90	30.5	0.02	[99]
$(C_3H_5)_4W+C_3H_5Cl$	0	9	91	10.1	0.12	[99]
$(C_3H_5)_4Zr$	61	4	35	34	0.02	[99]
$(C_6H_5CH_2)_4Ti$	15	25	60	27.5	0.02	[99]
π-RNiCl.chloranil	96	2	2	4.6	0.13	[100]
π-RNiCl·CCl$_3$C(H)(O)	93	6	1	4.6	0.13	[100]

*Solvent—THF.
**Solvent—benzene.

Although the mechanism of the formation of 1,2-units in coordination systems has not so far been studied experimentally, one may put forward certain considerations concerning the most probable pathway leading to the formation of syndiotactic structures under the influence of organomolybdenum, organotungsten, and organocobalt compounds, as well as organic derivatives of certain other metals[101]:

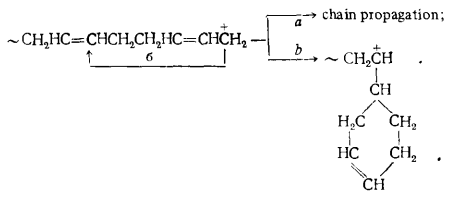


Complexes (I) and (II), formed alternatively in the course of chain propagation, differ sterically by the positions of the π-coordinating double bonds in the terminal unit of the polymer chain and the monomer. This chain propagation mechanism leads to a syndiotactic arrangement of units.

V. THE COPOLYMERISATION OF DIENES IN COORDINATION SYSTEMS

There is an antiparallel variation of the relative activities of dienes in cationic and anionic systems: chloroprene, butadiene, isoprene, *trans*-piperylene, cyclohexadiene, and 2,3-dimethylbutadiene. The reactivities increase in the above sequence when the active centres are cationic and decrease in polymerisation under the influence of anionic systems[97]. The above diene reactivity series in cationic systems is well illustrated by the increase of r_2 in the copolymerisation of isobutene (m_1) with dienes (m_2). The similarity of the copolymerisation constants r_1 and r_2 in the cationic copolymerisation of dienes with the corresponding olefins, for example, in the copolymerisation of butadiene with β-butene,[102] favours the development of cyclisation processes in the polymerisation and copolymerisation of

dienes:



In view of its high steric probability, reaction *b* takes place very vigorously even for low degrees of polymerisation and leads to cyclisation and loss of unsaturation.

In anionic copolymerisation, for example, under the influence of organometallic derivatives of alkali metals, the values of r_1 and r_2, reflecting the reactivity of the monomers, are consistent with the above sequence.

Table 8. The relative reactivities of the monomers (m) in coordination copolymerisation.

m_2	Catalytic system	Solvent	r_1	r_2	Refs.
		m_1—Butadiene			
Isoprene	$TiCl_4$ + (iso-C_4H_9)$_3$Al	benzene	1.00	1.00	[103, 104]
	TiI_4 + (iso-C_4H_9)$_3$Al	benzene	1.88	0.55	[105]
	$CoCl_2 \cdot C_2H_5OH$ + (iso-C_4H_9)$_2$AlCl	benzene	2.30	1.15	[103]
	$NiCl_2 \cdot Py$ + (C_2H_5)$_2$AlCl	benzene	1.15	0.59	[106]
	π-RNiCl + $TiCl_4$	toluene	6.20	1.15	[104, 107, 108]
	(π-RNiI)$_2$	toluene	0.30	2.35	[66, 109]
	π-R_2CrOSi|SiO_2	toluene	1.06	0.80	[62, 110]
	chromium oxide catalyst	toluene	1.04	0.76	[62, 110, 111]
	RLi	hexane	3.38	0.47	[105]
Cyclohexadiene	(π-RNiI)$_2$	toluene	0.80	1.10	[112]
	π-RNiCl·Ni(OCOCCl$_3$)$_2$	toluene	0.47	0.93	[113]
	π-RNiCl·A*	toluene	0.23—0.50	0.6—1.0	[113]
trans-Piperylene	(π-RNiI)$_2$	toluene	1.20	0.32	[82, 109]
	TiI_4 + R_3Al	toluene	3.60	0.50	[104, 107]
	$CoCl_2$ + R_2AlCl	toluene	1.20	0.30	[104, 107]
2,3-Dimethyl-butadiene	TiI_4 + R_3Al	toluene	6.30	0.15	[104, 107]
	$TiCl_4$ + R_3Al	toluene	2.16	0.33	[114]
	π-RNiCl.chloranil	toluene	2.80	0.18	[115]
	$CoCl_2$ + R_2AlCl	toluene	2.70	1.13	[114]
Styrene	π-RNiCl·A*	toluene	4.60	0.13	[100]
	RLi	benzene	10.00	0.035	[116]
	RCaI	benzene	10.00	0.04	[117]
		m_1—Isoprene			
Cyclohexadiene	(π-RNiI)$_2$	benzene	0.50	1.64	[118]
	$TiCl_4$ + LiR (1 : 1)	toluene heptane	0.30	0.80	[119]
	RLi	benzene	0.80	0.40	[119]
Piperylene	RLi	hexane	17±5	0.06	[120]
	$Ti(OR)_4$ + (C_2H_5)$_3$Al	benzene	0.30	0.30	[121, 122]
2,3-Dimethyl-butadiene	RLi	hexane	17.00	0.06	[120]

*A = acceptor.

The most important characteristic feature of the copolymerisation in coordination systems, particularly under the influence of organometallic compounds of transition metals, is the role of the coordination stage in the reactivity of the monomers. The probability of the incorporation of the monomer in the chain is determined both by the equilibrium in the coordination stage

$$RMX_n \overset{m_1}{\rightleftarrows} RMX_n + m_1; \quad RMX_n \overset{m_2}{\rightleftarrows} RMX_n + m_2$$

and by the rate of incorporation of the coordinated monomer in the chain. Since the "lifetime" of the terminal chain in the active centre depends on the rate of incorporation of the coordinated monomer (m_1 and m_2) in the chain, the rate of the *cis–trans* isomerisation of this unit should also vary in the copolymerisation process. The structure of the copolymers can therefore differ extremely significantly from that of homopolymers. Table 8 presents data for the relative reactivities of dienes in copolymerisation under the influence of various Ziegler systems and organonickel and organolithium compounds. It is seen from these results that the values of r_1 and r_2 depend greatly on the nature of the organometallic active centre. The copolymerisation in hydrocarbon media under the influence of RLi, where characteristics most typical for anionic systems are manifested, can serve as a comparison standard. Whereas the reactivity of butadiene (r_1) is much higher than those of isoprene, piperylene, and 2,3-dimethylbutadiene (r_2) in anionic systems, in systems of the Ziegler type the reactivities of the same pairs of monomers greatly approach one another, in some cases become identical, and in a few instances, for example in the copolymerisation of butadiene with isoprene or cyclohexadiene under the influence of π-RNiI, r_2 is much higher than r_1.

Table 9. The relative reactivities of the monomers (m) and the microstructure of the copolymers (m_1-butadiene, degree of conversion ~10%).

Catalytic system	m_2	[m_2], mole fraction	Contents of units in butadiene chain component, %			r_1; r_2	Refs.
			cis-	*trans*-	1,2-		
TiI_4 + R_3Al	isoprene	0	90	6	4	$r_1 = 2.8 \pm 0.2$; $r_2 = 0.53 \pm 0.05$	[104, 107, 108]
		0.30	49	37	12		
		0.66	41	40	19		
TiI_4 + R_3Al	2,3-dimethyl-butadiene	0.35	76	19	5	$r_1 = 6.3 \pm 0.2$; $r_2 = 0.15 \pm 0.06$	[104, 107, 108]
π-C_4H_7NiCl + $TiCl_4$	isoprene	0	90	8	2	$r_1 = 6.2 \pm 0.4$; $r_2 = 1.15 \pm 0.08$	[104, 107, 108]
		0.10	77	19	4		
		0.26	71	24	5		
		0.38	50	39	11		
π-C_4H_7NiCl + chloranil	2,3-dimethyl-butadiene	0	96.5	1.5	2	$r_1 = 2.8 \pm 0.3$; $r_2 = 0.18 \pm 0.05$	[115]
		0.14	87	7	6		
		0.28	78	13	9		
		0.51	64	20	16		
		0.72	40.5	37.5	21		

*Content of m_2 in the copolymer.

A second distinctive feature of the copolymerisation under the influence of coordination systems with participation of transition metals is the mutual influence of the monomers on the chain microstructure. The structure of the copolymers differs in most cases from that of the homopolymers obtained in the presence of the same catalysts. Under the influence of the second monomer (isoprene, piperylene, 2,3-dimethylbutadiene), participating in the copolymerisation, the *cis*-butadiene units in the copolymer are converted into the *trans*-units whose number is approximately equal to the content of the second monomer in the chain. This indicates a direct genetic relation between the conversion of the *cis*-butadiene unit into the *trans*-unit and the incorporation of

Table 10. The relative reactivities of the monomers (m) and the microstructure of the copolymers (m_1—butadiene).

Catalytic system	m_2	$[m_2]$, mole fraction*	Contents of units in butadiene component, %			r_1; r_2	Refs.
			cis-	*trans*-	1,2-		
π-RNiCl·A	cyclohexadiene	0 0.175 0.355 0.565	96 95.5 94.5 94.0	2 2 2.5 3.0	2 2.5 3.0 —	r_1=0.4—0.5; r_2=0.8—1.0	[113]
π-C_3H_5NiI	isoprene	0 0.50 0.83	0 0 0	95 96 91	5 4 9	r_1=0.30±0.04; r_2=2.35±0.15	[82, 109]
π-C_3H_5NiI	*trans*-piperylene	0.20 0.40 0.75	0 0 0	94 95 96	6 5 4	r_1=1.12±0.13; r_2=0.32±0.08	[82, 109]
π-$R_2CrOSi\|SiO_2$	isoprene	0.45 0.70 0.83	0 0 0	97 97 97	3 3 3	r_1=1.06; r_2=0.8	[62, 111]

*Content of m_2 in the copolymer.

the second monomer in the chain. Table 9 presents data for the copolymerisation of butadiene with other monomers under the influence of the *cis*-regulating TiI_4–R_3Al and π-RNiCl.A systems. Together with the increase of the content of the *trans*-butadiene units, a change in the microstructure of the isoprene and 2,3-dimethylbutadiene units incorporated in the chain towards an increase of the content of the *cis*-units is observed. In all the instances discussed, electron-donating additives (ethers, sulphides, and amines) exert the same influence on the butadiene homopolymer structure as the second comonomer in copolymerisation.

It is noteworthy that the rate of chain propagation decreases on passing from homopolymerisation to copolymerisation and, in the homopolymerisation of butadiene, also under the influence of added electron-donating compounds. In the copolymerisation of butadiene (m_1) with cyclohexadiene (m_2) under the influence of the complexes π-RNiX.A we have $r_2 > r_1$ and the *cis*-configuration of the butadiene units is fully retained in the copolymer[113]. The *trans*-configuration of the units is fully retained in the copolymers in the copolymerisation of butadiene with isoprene and of butadiene with piperylene under the influence of *trans*-regulating systems (π-RNiI, π-$R_2CrOSi|SiO_2$).[111] These postulates are illustrated by the data in Table 10.

In the copolymerisation of butadiene with other dienes in the presence of Ziegler systems containing active centres involving cobalt compounds, an inversion of stereoregulation is also observed under the influence of the second monomer, but it involves a change to 1,2-units and not *trans*-units, the number of the former corresponding approximately to the molar content of the second monomer in the chain. This is illustrated by the data in Table 11. Evidently, for approximately equal values of r_1 and r_2, isoprene and 2,3-dimethylbutadiene induce a sharp increase in the content of buta-1,2-diene units in the copolymer chain. Bearing in mind that the system based on cobalt compounds is used under certain conditions to synthesise crystalline 1,2-polybutadiene, presumably, on coordination of the second, more electron-donating monomer, the terminal butadiene unit passes to the σ-state, as in the mechanism proposed above for molybdenum and tungsten compounds. Electron-donating additives (ethers, sulphides, and amides), leading to an increase of the number of 1,2-units, exert a completely analogous influence on the microstructure of the butadiene homopolymer.

Table 11. The relative reactivities of the monomers (m) and the chain microstructure in copolymerisation under the influence of the $CoCl_2.C_2H_5OH$ + $(iso\text{-}C_4H_9)_2AlCl$ (m_1—butadiene) catalytic system[104,107,108].

m_2	$[m_2]$, mole fraction	Contents of units in butadiene component, %			r_1; r_2
		cis-	*trans*-	1,2-	
Isoprene	0 0.32 0.53	94 75 58	3 7 3	3 18 39	r_1=1.0±0.1; r_2=0.9±0.1
2,3-Dimethylbutadiene	0.27 0.41	44 26	7 6	49 68	r_1=0.74±0.02; r_2=0.67±0.05
trans-Piperylene	0.21 0.41 0.57	95** 80** 50**		5 20 50	

*Content of m_2 in the copolymer.
**Overall content of the *cis*- and *trans*-units.

It is noteworthy that in butadiene–isoprene copolymers the 3,4-units, whose content in the copolymer obtained in the presence of the "cobalt" system reaches 31%, have disappeared from the isoprene component of the copolymer chain. This means that only 1,4-isoprene units adjoin the butadiene units in the chain. In the butadiene–2,3-dimethylbutadiene copolymers the conversion of the *trans*-units of 2,3-dimethylbutadiene, adjoining the butadiene units, into the *cis*-units is observed. In the joint presence of the second monomer and an electron donor, a still more marked increase of the content of buta-1,2-diene units in the copolymer is observed. The rate of the process decreases

significantly in the presence of the second monomer or an electron-donating additive[104,107,108].

Studies in individual fields have been surveyed and published in other reviews[60,86,101,123–125].

VI. CONCLUSION

The investigations carried out have shown that the true active centres for the stereospecific polymerisation of dienes are individual organometallic compounds of transition metals. Chain propagation takes place as a result of the insertion of the monomer in the carbon–transition metal bond. The stereospecificity of the catalytic action is determined by the nature of the metal and the ligands surrounding it.

Experimentally supported hypotheses concerning the stereoregulation mechanism, according to which the structure of the polymer chain units is determined by that of the terminal unit in the active centre in the chain propagation stage, have been put forward. The specific features of coordination copolymerisation, distinguishing it from ionic and radical copolymerisation, have been determined.

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Institute of Petrochemical Synthesis,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 65-86 (1984) U.D.C. 541.64 : 547.315.2

Organometallic Catalysis in Diene and Cyclo-olefin Polymerisation Processes. II. The Metathesis Reaction in Polymer Chemistry

B.A.Dolgoplosk and Yu.V.Korshak

The development of ideas concerning the mechanism of the metathesis reaction and its employment in polymer chemistry are examined. The possible applications of the metathesis reaction in the synthesis of polymers by the polymerisation of cyclo-olefins and cyclodienes with ring opening and via the degradation of high-molecular-weight rubbers and their modification are discussed.
The bibliography includes 160 references.

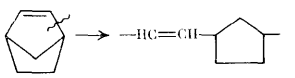
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I. THE MECHANISMS OF REACTIONS INVOLVING RING OPENING IN CYCLO-OLEFINS AND METATHESIS REACTIONS OF OLEFINS

The polymerisation of norbornene under the influence of the $TiCl_4$–$Al(C_7H_{13})_4$ catalytic system with formation of a polymer in which the double bonds of the initial monomer are fully retained was first carried out in 1955–1956.[1-3] Subsequently Natta and other investigators[4-8] demonstrated the possibility of synthesising analogous linear polymers from cyclopentene, cyclo-octadiene, and other cyclo-olefins with the aid of catalytic systems containing tungsten or molybdenum compounds and organoaluminium compounds. The compositions of the above systems resemble those of the Ziegler catalysts for the polymerisation of olefins and dienes.

Truett and co-workers[2,3], who investigated this reaction with respect to norbornene, concluded that the ring opening in the polymerisation of norbornene takes place at the C–C bond adjoining the double bond:



Natta and co-workers, who studied the polymerisation of a series of cyclo-olefins with ring opening, initially adopted an analogous view as to the reaction mechanism[9].

Studies on the redistribution of double bonds in olefins under the influence of catalysts containing molybdenum and tungsten compounds in combination with alkylating agents developed independently and simultaneously. In 1964 Banks and Bailey[10] demonstrated for the first time that, when propene is maintained over MoO_3 or WO_3 on Al_2O_3 at 120 °C and a pressure of 35 atm, small amounts of ethylene and butene are formed. Subsequently many other catalytic homogeneous and heterogeneous catalytic systems, incorporating tungsten, molybdenum, rhenium, or tantalum compounds in combination with alkylating agents (particularly with organoaluminium or organotin compounds) were put forward[11-22]. In homogeneous systems the reaction involving the redistribution of double bonds in many olefins takes place at very high rates without heat changes at normal temperatures[23,24].

In a number of studies[24-26] using ^{14}C-labelled and deuteriated olefins it was shown experimentally that the olefin disproportionation reaction proceeds via the direct rupture of the double bonds. For example, this has been demonstrated[24] for the cometathetical reaction of but-2-ene and perdeuterobut-2-ene:

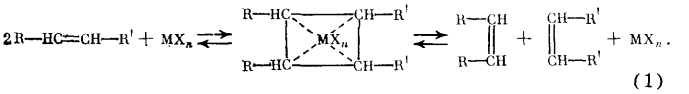
$$CH_3HC{=}CHCH_3 + CD_3DC{=}CDCD_3 \rightleftarrows 2CH_3HC{=}CDCD_3 \quad .$$

On the basis of a study of the composition of the decomposition products of ozonised copolymers of ^{14}C-labelled cyclopentene with cyclo-octene, Dall'Asta and Montroni[27] showed that the polymerisation of cyclo-olefins with ring opening also proceeds with the rupture of the double bonds and that its character is analogous to that of the reaction of olefins under the influence of the same catalytic systems. Subsequently the term "metathesis reactions" was proposed for the reactions of the given type proceeding via a stage involving the dissociation of multiple carbon–carbon bonds.

Reviews have been devoted to various aspects of the metathesis reactions[28-37]. Table 1 presents the compositions of the catalytic system used for the polymerisation of cyclo-olefins.

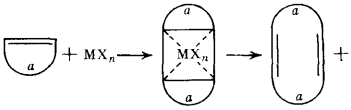
1. Development of Ideas about the Process Mechanism

In order to account for the mechanism of the metathesis reactions of olefins, Bradshaw et al.[38] introduced the concept of an intermediate consisting of a quasi-cyclobutane ring made up of two olefin molecules in which all the carbon atoms are linked by equivalent bonds to the transition metal:



(1)

Scott[39] applied these ideas to ring opening in cyclo-olefins:



(2)

Eqns.(1) and (2) presuppose a stepwise process with formation of oligomeric cyclo-olefin polymerisation products in the initial stages in the latter case. It has been noted[40] that these ideas conflict with the formation of high-molecular-weight products in polymerisation processes, which enabled the authors[40] to put forward certain considerations concerning the chain nature of the process involving carbene complexes.

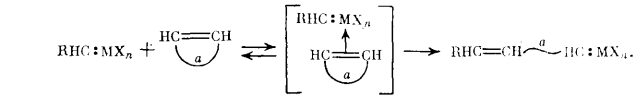
Systematic investigations[41–44] have shown that, even for a low degree of conversion of cyclo-olefins (cyclopentene, norbornene, cyclo-octene, and cyclo-octadiene), high-molecular-weight products are formed. In certain systems the intrinsic viscosity of the polymers formed in the initial stages of the process reached 7–9. These results yielded the unambiguous conclusion that the process has a chain mechanism[40–42,45,100]. As will be shown below, the formation of a small amount of oligomers in certain cases is due to the development of the reverse cyclodegradation process.

Table 1. Catalytic metathesis systems active in the cyclo-olefin ring opening reaction.

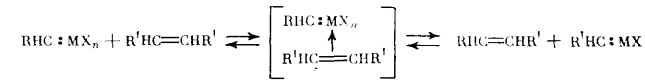
Transition metal compound (A)	Alkylating agent (B)	[A]/[B], mol mol^{-1}	Cyclo-olefin	Refs.
		Heterogeneous systems		
$MoO_3\|Al_2O_3$	$LiAlH_4$	—	Cyclopentene	[11]
$CoO—MoO_3\|Al_2O_3$	—	—	Cyclo-octene	[12, 13]
$Re_2O_7\|Al_2O_3$	—	—	Cyclo-octene, cyclopentene	[14]
		Homogeneous systems		
$TiCl_4$	C_2H_5MgBr	2/1	Norbornene	[1]
$TiCl_4$	$LiAl(C_3H_7)_4$	3/1÷5/1	Norbornene	[3]
$(NH_4)_2IrCl_6$; $RuCl_3$	$SnCl_2$; Zn+CH_3COOH	—	Norbornene derivatives	[17]
$MoCl_5$	$Al(C_2H_5)_3$	2 5/1	Cyclobutene, cyclopentene	[4, 5]
WCl_6	$Al(C_2H_5)_3$	2.5/1	Cyclopentene	[5]
WCl_6	$Al(C_2H_5)Cl_2$	5/1	Cycloheptene,	[6]
WF_6	$Al_2(C_2H_5)_3Cl_3$	7/1÷1/2	Cyclo-octene	[18]
$MoCl_2\cdot 2P(C_6H_5)_3(NO)_2$	$Al(CH_3)Cl_2$	10/1	Cyclopentene	
$WCl_2\cdot 2P(C_6H_5)_3(NO)_2$	$Al_2(CH_3)_3Cl_3$	10/1	Cyclopentene	[19, 20]
$(CO)_5W=C(C_6H_5)_2$	—	—	Cyclo-octene	[21]
$TaCl_5$	$LiCH_2Si(CH_3)_3$	1/1	Cyclo-octene	[16]

The possibility of the initiation of the cyclo-olefin polymerisation reaction by the decomposition products of diazo-compounds arising when the latter interacts with WCl_6 and $MoCl_5$ constitutes direct experimental proof of the carbene nature of the active centres[46,47]. Phenyldiazomethane, diazoacetate, and trimethylsilyldiazomethane, which are decomposed catalytically under the influence of tungsten and molybdenum halides with the liberation of nitrogen and the formation of carbene complexes, were used as the initial diazo-compounds.

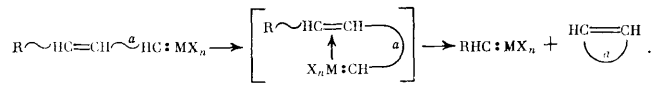
The results obtained served as a basis for the consideration of the reaction mechanism[40,45]. The scheme presented below presupposes the coordination of the monomer to the transition metal attached to a carbene species and its incorporation into the chain with regeneration of the carbene complex:



An analogous mechanism has been proposed for the metathesis of olefins:



Since the polymer chain formed in the polymerisation of cyclo-olefins retains the double bonds, the latter can participate in metathesis reactions. When the growing carbene active centre interacts with a double bond in its own chain, a cyclodegradation reaction, which leads to the formation of cyclic oligomeric molecules, takes place:



The contribution of these reactions in the polymerisation of cyclo-olefins increases as the monomer concentration diminishes, which leads to the formation of oligomers and to the broadening of the molecular weight distribution (MWD) of the polymer. Fig. 1 presents data illustrating the variation of the MWD with the degree of reaction[48].

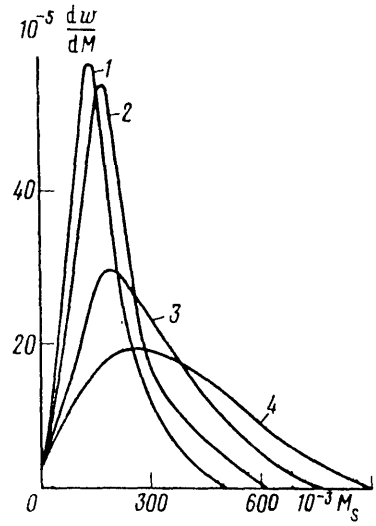


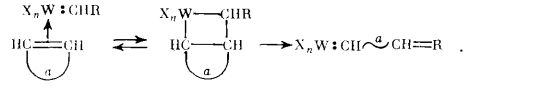
Figure 1. The molecular weight distribution of cyclo-octa-1,5-diene (COD) polymers obtained for different degrees of conversion; [COD] = 0.9 M; [Al]/[W] = 5/1; [COD]/[W] = 800/1; 20 °C in toluene. Degree of conversion (%): 1) 19; 2) 25; 3) 31; 4) 44.[48]

If there is no monomer in the system, then, as will be shown below, the same catalysts induce the cyclodegradation of unsaturated polymers in solution. The idea that the process has a chain mechanism (via stages involving the formation of carbene complexes) was subsequently confirmed by a number of other investigators[49–51] and is at present generally accepted.

On the grounds that metallocyclobutane compounds of the type



initiate the ring opening in cyclo-olefins, the authors of a number of studies suggested that the chain propagation stage can proceed via similar intermediates[49,51,53–56]:

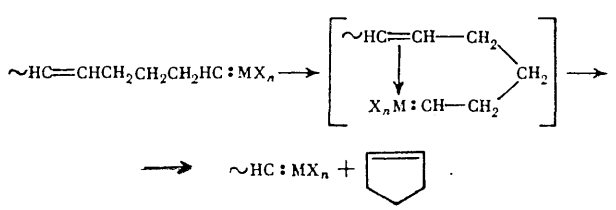


This hypothesis appears to us unlikely, since the rate of chain propagation exceeds by several orders of magnitude the rate of initiation by such organometallic compounds. Furthermore, one should note that the decomposition of compounds of this kind at low temperatures proceeds via carbene formation stages[57].

In a number of studies devoted to the reactions of stable carbene complexes of tantalum and niobium incorporating olefins, the formation of intermediate unstable metallocyclobutane species has been postulated[58,59]. However, the decomposition of these intermediate compounds proceeds via the usual β-elimination pathway and leads to various isomers of linear olefins containing the initial carbene fragment. An extremely striking feature is that the products of the metathetical reaction were not detected in the instances considered[22,58], but in a number of reactions it was possible to isolate a metallocyclopentane complex formed as a result of the cycloaddition of two molecules of the initial olefin to the transition metal compound[60]. Similar metallocyclopentane complexes had been considered earlier as intermediates in the metathesis reaction[61], but in subsequent studies by Grubbs and co-workers[62] and Schrock and co-workers[63,64] it was shown that the cyclopentane derivatives of tantalum and niobium are effective catalysts of the selective dimerisation of various olefins and show no activity in the metathesis reaction.

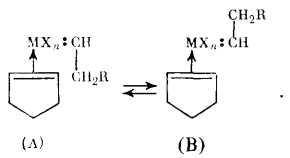
The polymerisation of cyclo-olefins under the influence of metathesis catalysts is a reverisble process which in the case of cyclopentene leads to a polymer–monomer equilibrium, while in the case of other cyclo-olefins a polymer–oligomers equilibrium obtains. The position of equilibrium in a polymerisation reaction for *trans*- and *cis*-polypentenamers is characterised by the data in Fig. 2.[65,66]

For the *cis*-conformation of the units of the polypentenamer, the equilibrium content of the monomer in solution is significantly higher than for the *trans*-polypentenamer, which is apparently due to the greater steric mobility of the coordination of the active centre to the double bond of the neighbouring unit:



The ratio of the *cis*- and *trans*-units in the cyclo-olefin polymers depends significantly on the nature of the catalytic system and the polymerisation temperature. Table 2 presents data characterising the microstructure of the chain in polypentenamers obtained in the presence of various catalytic systems and at various temperatures.

The initial cyclo-olefins are characterised in most cases by the *cis*-conformation of the units (cyclobutene, cyclopentene, norbornene, cyclo-octadiene, and cyclo-octene); the formation of *trans*-units in the polymer must therefore be associated with isomerisation steps. It has been suggested[69] that the isomerisation may be due to the rotation of the carbene active centre. The energy of rotation about the C : M bond for various carbenes bound in complexes with tantalum compounds is 12–22 kcal mole^{-1}.[70] For systems active in metathesis reactions, these values may be significantly lower. It is most likely that the rotations about the C : M carbene bond are executed at the instant of the coordination of the monomer to the transition metal:



The state (A) leads to the *cis*-unit and the state (B) to the *trans*-unit. The very marked temperature dependence of the ratio of the *cis*- and *trans*-units in the polypentenamer (Table 2) indicates a low activation energy for the *cis*–*trans* rotations of the carbene active centre. A similar temperature dependence, albeit less marked, has been observed also for other cyclo-olefins.

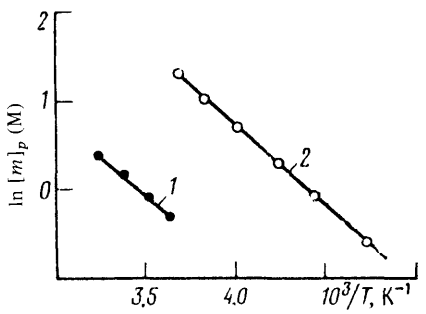


Figure 2. Temperature variation of the equilibrium monomer concentration $[m]_p$ in the cyclopentene–polypentenamer system: 1) *trans*-polypentenamer[65]; 2) *cis*-polypentenamer[66].

Table 2. The influence of temperature and catalyst on the structure of cyclopentene polymers.

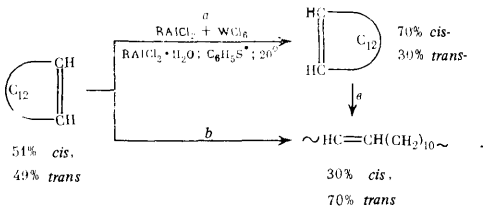
Catalytic system	*t*, °C	Content of units, %		Refs.
		cis-	*trans*-	
WCl_6–C_2H_5OH–$Al(C_2H_5)Cl_2$	+20	20	80	[65]
WCl_6–$(C_2H_5)_2O$–$Sn(C_2H_5)_4$	−30	80	20	[67]
Ditto	0	30	70	[67]
»	+30	18	82	[67]
WCl_6-tetra-allylsilane	−40	100	0	[66]
Ditto	0	76	24	[66]
»	+20	40	60	[66]
$MoCl_5$–$Al(C_2H_5)_3$	+20	100	0	[5]
$MoCl_5$–$(C_4H_9Cl)_2O$–$Sn(C_2H_5)_4$	+20	18	82	[68]
WF_6–$Al(C_2H_5)Cl_2$: Al/W = 1/2	−30	85	15	[18]
Al/W = 7/1	+30	10	90	[18]

In the catalysis of metathesis by systems incorporating tungsten compounds, tungsten atoms in a valence state ranging from zero to 4–5 are apparently involved. An example of the participation of zero-valent tungsten is the initiation of polymerisation under the influence of $(CO)_5W : C(C_6H_5)_2$.[21]

In the usual systems containing $RAlCl_2$ and WCl_6 tungsten is in the (4–5)-valence state[71]. An example of the initiation of metathesis under the influence of Mo^{2+} is provided by the

$MoCl_2.2NO.(C_6H_5)_3P-RAlCl_2$ system[20]. Catalytic systems containing Mo^{4+} are also effective[72]. In the stable Fischer carbenes the valence of the metal is always zero or 1, and the carbene species contain as a rule one or two heteroatoms (O, N, or S) at the carbene carbon atom. These factors and also the presence of stabilising ligands (CO, phosphine groups, etc.) at the metal atoms are responsible for the stability of the carbene complexes. It has been shown[73] in relation to chromium complexes that some of them can be used in metathesis reactions.

Since the rate of chain propagation depends greatly on the nature of the metal and the ligands surrounding it, this is reflected correspondingly also in the chain microstructure; the higher the rate of propagation the smaller the contribution of the *cis–trans* isomerisation of the active centre. The *cis–trans* isomerisation can occur also in the polymer chain under the influence of the components of catalytic systems. Thus it has been shown for cyclododecane containing a non-equilibrium proportion of molecules in the *cis*- and *trans*-conformations that it isomerises under the influence of metathesis catalysts, cationic systems, and C_6H_5S radicals[74]:



Reaction *a*, leading to a state of equilibrium of cyclododecene, is much faster than reaction *b*. The equilibrium content of the *cis*- and *trans*-units, characteristic of linear olefins, is therefore found in the polymer chain obtained at room temperature.

As in all other chain polymerisation processes, in the reactions considered very small amounts of compounds leading to the formation of carbene species more stable than the growing chain species partially or completely inhibit the polymerisation. Thus, in the polymerisation of cyclopentene in the presence of metathesis catalysts, very small amounts of alkyl vinyl ethers, alkyl vinyl sulphides, and trimethylvinylsilane fully inhibit the polymerisation reaction[75–77]:

$$\sim HC{=}CH(CH_2)_3HC{:}MX_n + H_2C{=}CHXR \rightarrow RXHC{:}MX_n + \sim HC{=}CH(CH_2)_3HC{=}CH_2;$$
$$X = O, S, Si .$$

The presence of a heteroatom at the carbene active centre is known to entail the stabilisation of the carbene, which renders energetically unfavourable its participation in the opening of the cyclopentene ring, since it leads to the formation of a more active carbene species. The above considerations are correlated with the finding that the efficiency of the initiation by diazo-compounds decreases in the sequence

$$C_6H_5CHN_2 > RO{-}CO{-}CHN_2 > (CH_3)_3SiCHN_2 .$$

The compound $(C_6H_5)(C_6H_5CO)CN_2$, leading to the formation of the stable carbene $(C_6H_5)(C_6H_5CO)C:MX_n$, does not initiate polymerisation[78].

The chain character of the process and the decisive role of the reactivity of the carbene species in its kinetics can be illustrated also in relation to the metathesis of olefins. It has been shown[79–81] that a degenerate metathesis reaction of α-olefins [reaction (3)] is 10^2–10^3 faster than reaction (4):

$$RHC{=}CH_2 + R'HC{=}CD_2 \begin{cases} \rightarrow RHC{=}CD_2 + R'HC{=}CH_2 , & (3) \\ \rightarrow RHC{=}CHR' + H_2C{=}CD_2 . & (4) \end{cases}$$

The cause of this phenomenon has been explained[58,82]. Pathway (3) occurs as a result of the alternate exchange of the secondary carbene complexes with similar reactivities:

$$R'HC{:}MX_n \rightarrow RHC{:}MX_n \rightarrow R'HC{:}MX_n \text{ etc.}$$

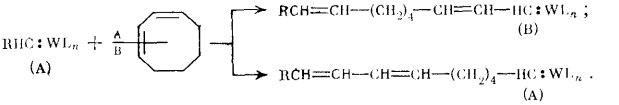
Reaction (4) can proceed only via consecutive stages involving the formation of secondary and primary carbene complexes:

$$R'HC{:}MX_n \underset{\downarrow}{\uparrow} H_2C{:}MX_n \underset{\downarrow}{\uparrow} RHC{:}MX_n \underset{\downarrow}{\uparrow} D_2C{:}MX_n \underset{\downarrow}{\uparrow} R'HC{:}MX_n \text{ etc.}$$

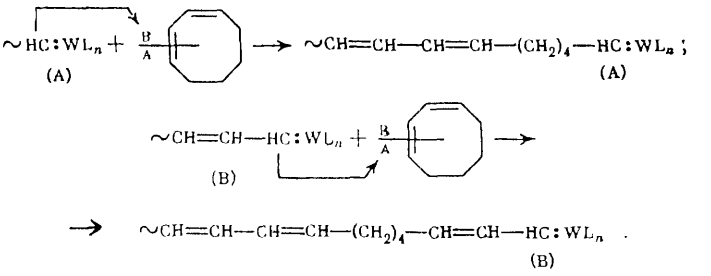
Under the conditions of the chain process, in which the length of the kinetic chain reaches 10^5–10^7, even small differences between the reactivities of the primary and secondary carbene complexes lead to a marked retardation of the reaction. These features are fully analogous to those of the free radical reactions of olefins.

An interesting case of the involvement of conjugated dienes in a metathesis reaction has been investigated[83]. It was shown that cyclo-octa-1,3-diene polymerises in the presence of the $Cl_4W[OCH(CH_2Cl)_2]_2-Al(C_2H_5)_2Cl$–dibutyl ether systems; up to a degree of conversion of the monomer of 30%, the process occurred with formation of a high-molecular-weight soluble polymer. The fairly high effectiveness of cyclo-octa-1,3-diene in the polymerisation reaction is apparently due to the displacement of the double bonds in its molecule from coplanarity[84]. The polymer obtained contained conjugated diene groups, which, in contrast to the initial monomer, readily underwent the Diels–Alder reaction, forming reactive adducts.

In contrast to cyclo-olefins and non-conjugated cyclodienes, in the polymerisation of cyclo-octa-1,3-diene there is a possibility of the formation of two different types of carbene centres differing in their reactivities[83]:

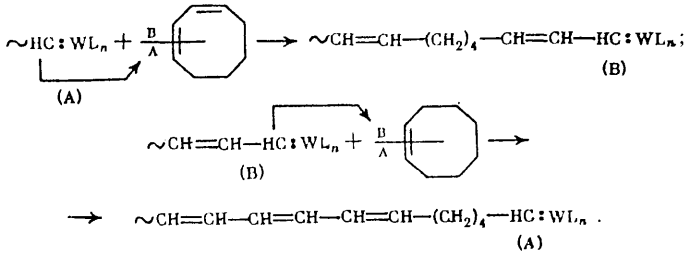


The "head-to-tail" chain propagation should involve the formation of a polymer containing regularly alternating diene sequences. In this case, after each addition of an alternate cyclo-octa-1,3-diene molecule, an active centre of the same type is regenerated (A or B):



However, the presence of triene and isolated –C=C– bonds in the cyclo-octa-1,3-diene polymers together with diene bonds indicates the occurrence of interconversions of the non-conjugated carbene centre (A) and the carbene centre

(B) conjugated with a double bond:



The conversion of the non-conjugated carbene centre into the more stable conjugated centre, (A) → (B), is energetically more favourable, which leads to the preferential formation of diene sequences in the polymer.

The molecular weight characteristics and the MWD of cyclo-octa-1,3-diene polymers have been investigated[48] and it has been shown that, up to a degree of polymerisation of 35%, the molecular weight of the polyoctadienamer increases linearly with the degree of conversion, which is consistent with the mechanism of the propagation of "live" chains. Fig.1 shows that the polymers obtained initially have a narrow molecular weight distribution with a polydispersity coefficient of 1.25 to 1.30. The equality of the polydispersity coefficients found ($\bar{M}_W/\bar{M}_n \cong \bar{M}_Z/\bar{M}_W$) as well as the form of the MWD curves confirm the fact that the cyclo-octa-1,5-diene polymers investigated (polyoctadienamers) have a molecular weight distribution close to the Poisson distribution.

Analogous results have been obtained for polypentenamer specimens obtained in the presence of the $Cl_3Mo(stearate)_2$–$Al(C_2H_5)_2Cl$ system, as shown by Pakuro et al.[86] This demonstrates the occurrence of a polymerisation process without termination in the presence of the systems indicated. It is noteworthy that a very small number of the active centres, in which the carbene species are stabilised by coordination to the transition metal atom, participate in the polymerisation reaction. For a number of other catalytic systems, a broad MWD is observed in the initial stage of the process, which may be associated both with the low rate of the initiation stage[87,88] and with chain termination.

As in the case of typical Ziegler catalysts, chain termination in the metathesis reaction can occur as a consequence of the presence of various admixtures (water, alcohols, etc.) in the reaction systems. However, complete termination of the chain metathesis process is also possible as a result of side reactions leading to the destruction of the carbene species. This applies particularly to reactions involving insertion into the C–H, C–C, and C=C (the formation of cyclopropane groups) bonds, as well as other reactions characteristic of free carbenes.

The unstable carbene complex $(CO)_5W:C\begin{smallmatrix}H\\C_6H_5\end{smallmatrix}$ has been obtained[89]; by reacting at the instant of formation with various α- and β-olefins, it gave rise to cyclopropane derivatives in a yield up to 98%. An analogous reaction involving conversion into cyclopropane derivatives has been described for the stable carbene complexes of chromium and iron[90,91]. This reaction is undoubtedly one of the possible variants of chain termination in metathesis, which was first noted by Dolgoplosk et al.[40] On the basis of quantum-chemical calculations for various intermediate states of the carbene complexes of tungsten, molybdenum and chromium, Rappe and Goddard[92] concluded that in the case of chromium this termination pathway is dominant and that this explains the low activity of chromium in metathesis reactions.

2. Generation of Carbene Active Centres in the Decomposition of Organometallic Compounds of Transition Metals

The question of the pathways leading to the formation of carbene active centres initiating the metathesis reaction remained least clear. Since the primary step in metathesis systems always leads to the formation of an organometallic compound, only the decomposition of such a compound can serve as a source of carbenes. Schrock and co-workers[93–95] showed that stable carbene species are formed on decomposition of pentabenzyltantalum and pentaneopentyltantalum:

$$(C_6H_5CH_2)_5Ta \rightarrow (C_6H_5CH_2)_3Ta:CHC_6H_5 ,$$
$$[(CH_3)_3CH_2]_5Ta \rightarrow [(CH_3)_3CH_2]_3Ta:CHC(CH_3)_3 .$$

The ways in which carbene species arise on decomposition at the instant of the formation of various organometallic compounds of transition metals have been investigated in greatest detail by Dolgoplosk and co-workers[97–99,101]. The $(CH_3)_3.SiCH_3Li$–WCl_6 system proved to be effective for the polymerisation of cyclopentene at temperatures down to −78 °C. The reaction of $(CH_3)_3SiCH_2Li$ with tungsten and other transitional metal halides in the absence of a monomer can proceed via the following main pathways:

$$(CH_3)_3SiCH_2MCl_n \rightarrow (CH_3)_3SiCl + H_2C:MCl_{n-1} ; \quad (5)$$

$$[(CH_3)_3SiCH_2]_2MCl_{n-1} \rightarrow (CH_3)_4Si + (CH_3)_3SiHC:MCl_{n-1} ; \quad (6)$$

$$[(CH_3)_3SiCH_2]_2MCl_{n-1} \rightarrow (CH_3)_3Si{-}CH_2CH_2Si{-}(CH_3)_3 + MCl_{n-1} . \quad (7)$$

Reaction (5) leads to the formation of methylene carbene; its contribution can be estimated from the yield of $(CH_3)_3SiCl$. The contribution of reaction (6) can be estimated from the yield of $(CH_3)_4Si$, since it has been shown that the formation of $(CH_3)_3SiCH_2D$ is not observed in the products of the reaction when the latter is carried out in a perdeuteriated solvent. The experimental data are listed in Table 3. These questions have been examined in greatest detail by Dolgoplosk[15].

Table 3. Composition of the products of the interaction of $(CH_3)_3SiCH_2Li$ with MCl_n.

MCl_n	RLi/MCl_n, mol mole^{-1}	Yield, % of theoretical			Overall group balance, %	Refs.
		$(CH_3)_4Si$	$(CH_3)_3SiCl$	R–R*		
WCl_6	1.0	17	31	—	90	[98]
WCl_6	2.0	23	23	—	95	[16]
$MoCl_5$	2.0	31	10	14	86	
$TaCl_5$	0.5	43	10	traces	96	[16]
$TaCl_5$	1.0	35	12	traces	93	[16]
$ReCl_5$	0.5	7	9	81	105	[102]
$ReCl_5$	1.0	20	5	55	100	[102]

*Recombination product.

When metal (W, Mo, Ta, Re, or Nb) halides are used, a considerable number of methylene species, which are the most active in the initiation of metathesis reactions, are formed. The formation of a considerable amount of tetramethylsilane in all cases proves that carbenes of the type $(CH_3)_3SiCH$: play a role; as shown in the decomposition of $(CH_3)_3SiCHN_2$, these carbenes are also involved in the initiation of the metathesis reaction but with a lower efficiency. Twice the amount of the $(CH_3)_4Si$ found, $(CH_3)_3SiCl$, and the groups forming part of the composition of the R–R products enter into the overall group balance.

In the case of the $(CH_3)_3GeCH_2Li$–WCl_6 system, the reaction involving the formation of methylene carbene predominates (up to 50% of the total amount of the groups which have reacted[98]). The decomposition of trideuteromethyl derivatives of tungsten and molybdenum in dibutyl ether proceeds analogously[101]. The main decomposition products are CD_3CD_3, $CD_2{=}CD_2$, and CD_4. The yield of CD_4 is 60 to 70% mole in the case of $MoCl_5$, which shows that the reaction leads to the formation of carbynes:

$$(CD_3)_2\,MoCl_3 \rightarrow CD_4 + D_2C{:}\,MoCl_3\ ;$$
$$(CD_3)_3\,MoCl_2 \rightarrow 2CD_4 + DC{\vdots}\,MoCl_2\ .$$

Carbene, carbyne, and carbide species bound to the metal have been found in the reaction products. For all the metal halides quoted above, the reaction with benzylmagnesium chloride takes place analogously in diethyl ether at 20 °C.[104] The fraction of carbene species can be estimated from the yield of toluene, because, when the reaction was carried out in perdeuterodiethyl ether, the formation of appreciable amounts of $C_6H_5CH_2D$ was not observed:

$$(C_6H_5CH_2)_2\,MX_n \rightarrow C_6H_5CH_3 + C_6H_5HC{:}\,MX_n\ ;$$
$$(C_6H_5CH_2)_3\,MX_{n-1} \rightarrow 2C_6H_5CH_3 + C_6H_5C{\vdots}\,MX_{n-1}\ .$$

Table 4 presents the compositions of the reaction products.

Table 4. Composition of the products of the interaction of benzylmagnesium chloride with metal halides in ethyl ether at 20 °C.

MCl_n	$RMgCl/MCl_n$, mol mole^{-1}	Yield, % of theoretical				Refs.
		toluene	stilbene	tolane	bibenzyl	
$MoCl_5$	3	14—16	0.8—1.5	0.3—0.7	25—27	[104]
WCl_6	4	17.7	0.5	0	19.1	[103]
$ReCl_5$	3	22—27	1.7—2.0	0	18—20	[103]

Thus the carbene pathway to the decomposition is characteristic not only if the compounds of the metals used in metathesis reactions but also of many other transition metals widely employed in heterogeneous and homogeneous catalysis. In the tetra-allylsilane–WCl_6 system[105,106], recommended for the synthesis of *cis*-polypentenamer by the polymerisation of cyclopentene at −30 °C, the reaction leads to the generation of considerable amounts of propene:

$$(H_2C{=}CHCH_2)_2\,WCl_4 \rightarrow CH_3HC{=}CH_2 + H_2C{=}CHHC{:}\,WCl_4\ .$$

The polymerisation of cyclopentene is apparently initiated by the vinylcarbene complex. The catalytic systems usually consist of alkyl derivatives of aluminium or tin and tungsten and molybdenum halides. It is well known that the alkyl derivatives of transition metals decompose via the β-elimination pathway:

$$(CH_3CH_2)_2\,MX_n \rightarrow H_2C{=}CH_2 + H_3C{-}CH_3\ .$$

So far there are no direct ways of investigating the contribution of α-decomposition in the systems indicated, which leads to a formation of carbene active centres. However, experimental studies have shown that α-decomposition also takes place in the systems considered:

$$(CH_3CH_2)_2\,MX_n \rightarrow H_3C{-}CH_3 + CH_3HC{:}\,MX_n\ .$$

When the reaction was carried out with WCl_6 and $MoCl_5$ in the presence of trimethylvinylsilane, the formation of appreciable amounts of propene was observed[107,108]. Since the presence of the silicon atom at the carbene active centre greatly stabilises the latter, the chain transfer reaction

$$CH_3HC{:}\,MX_n + H_2C{=}CHSi(CH_3)_3 \rightarrow (CH_3)_3SiHC{:}\,MX_n + CH_3HC{=}CH_2$$

becomes energetically favourable.

The data obtained illustrate only qualitatively the α-decomposition reactions, since the carbenes formed in this process largely disappear as a result of side reactions with the solvent and only a small fraction of the carbenes, stabilised as a result of coordination to the transition metal, are involved in polymerisation.

In the analysis of the nature of the transition metal–carbene bond, Rappe and Goddard[92] concluded that it depends significantly on the valence state of the metal. Quantum-chemical calculation has shown that this bond is covalent for transition metal complexes in higher oxidation states and is mainly of the coordinate type (with a low barrier to rotation) for the more reduced forms of the metal, for example in the complex $(C_5H_5)_2TaCH_2(CH)_3$.[22,70]

II. THE DEGRADATION OF POLYMERS UNDER THE INFLUENCE OF METATHESIS CATALYSTS

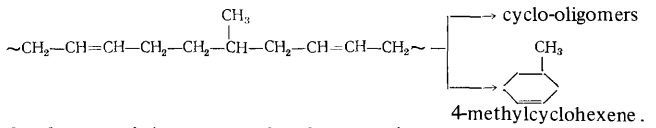
1. Cyclodegradation of Polyalkenamers

It has been shown for the first time in a number of studies[109–111] that *cis*-polybutadiene undergoes rapid degradation in solution under the influence of metathesis catalysts at room temperature. The chain character of this process has been demonstrated[112] by carrying out the reaction in dilute (1%) solution of *cis*-polybutadiene in the presence of minimal amounts of the catalyst. In this case the carbene active centres arise only on individual polymeric molecules and intramolecular chain transfer reactions mainly develop as a consequence of the low polymer concentration. The study of the reaction products demonstrated the constancy of the MWD of the high-molecular-weight polybutadiene in the simultaneous presence in the system of oligomeric products formed on decomposition of the individual polybutadiene molecules. Thus this process, which occurs at room temperature, is of the same chain character as the radical depolymerisation reactions of polystyrene and poly(methylacrylates) at high temperature. In the last two processes the initial monomer is formed preferentially, while the products of metathesis reactions are cyclic oligomers arising as a result of chain transfer with rupture.

In certain cases the degradative cyclisation reaction of polyalkenamers leads to the formation of cyclo-olefins, which has been demonstated for polypentamer[65] and an alternating propene–butadiene copolymer[113]. The degradative cyclisation of polypentamer and the character of the variation of the MWD under the influence of the WCl_6–tetramethyldisilacyclobutane system, active in the metathesis reactions in linear olefins, have been investigated[87,88]. The degradation of polypentamer (72–83% of *trans*-units) was carried out at 20 °C at a polymer concentration below the equilibrium monomer concentration at the given temperature (equal to 0.88 M for the formation of *trans*-polypentamer). Under these conditions, the degradation proceeds with 100% conversion of polypentenamer into cyclopentene:

$$-[-CH_2-CH{=}CH-CH_2-CH_2-]_n- \rightarrow n\,\square\ .$$

The degradation of the alternating butadiene–propene copolymer under the influence of the $Cl_4W[OCH(CH_2Cl)_2]_2$–$AlC_2H_5Cl_2$ system takes place with formation of cyclo-oligomers, which are subsequently converted into 4-methylcyclohexene (yield above 90%):[113,160]



4-methylcyclohexene.

In the remaining cases the degradation of unsaturated polymers leads to cyclic oligomeric products. The degradative cyclisation of linear *cis*-polybutadiene and *cis*-polyoctadienamer in the presence of tungsten-containing catalysts is accompanied by an appreciable *cis-trans* isomerisation of the double bonds (Table 5).

Table 5. Degradative cyclisation of *cis*-polyalkenamers in solutions at 20 °C.

Catalyst	*c*, wt.%	τ, min	Initial polymer		Oligomers		α, %		Refs.
			$\bar{M}_n$	$[\eta]$, dl g^{-1}	$\bar{M}_n$	$[\eta]$, dl g^{-1}	α^P, %	α^O, %	
Polybutadiene									
WCl_6–$C_2H_5AlCl_2$	4	20	127 000	—	3 400	—	92	—	[109]
Ditto	8	25	220 000	—	9 000	—	92	—	[109]
»	8	30	220 000	—	10 000	—	92	—	[109]
$MoCl_3$(stearate)$_2$–$(C_2H_5)_2AlCl$	10	15	200 000	—	3 680	—	92	92	[108]
Ditto	10	75	200 000	—	1 400	—	92	91	[108]
$WCl_4(OR)_2$–$C_2H_5AlCl_2$	8	20	—	2.5	—	0.24	95	82	[114]
Ditto + Δ	8	40	—	2.5	—	0.17	95	47	[114]
Polyoctadienamer									
$WCl_4(OR)_2$–$C_2H_5AlCl_2$	8	3	—	2.0	—	0.30	85	60	[114]
Ditto	8	30	—	2.0	—	0.24	85	55	[114]
Ditto + Δ	8	68	—	2.0	—	0.20	85	30	[114]
Polyisoprene*									
$WCl_4(OR)_2$–$(C_2H_5)_2AlCl$–anisole	6	12	—	5.9	—	0.95	97	97	[115]
Ditto	6	24	—	5.9	—	0.75	97	97	[115]
»	6	120	—	5.9	—	0.39	97	97	[115]

Notation: *c* is the polymer concentration, α^P and α^O are the contents of *cis*-units in the polymer and oligomer respectively, and Δ is a fresh portion of the catalyst.

*For the polyisoprene degradation processes, the time is given in hours.

The use of the $MoCl_3(stearate)_2$–$(C_2H_5)_2AlCl$ molybdenum-containing systems makes it possible to achieve a far-reaching degradation of *cis*-polybutadiene with retention of the *cis*-configuration of the double bonds in the cyclo-oligomers. After 15–20 min have elapsed from the start of the reaction, the molecular weight of polybutadiene diminishes by a factor of approximately 100 and the system rapidly attains a state close to equilibrium, as shown by the constant molecular weight, i.e. the intrinsic viscosity $[\eta]$, after the addition of a fresh portion of the catalyst. The study of the polydispersity of the cyclo-oligomers obtained indicates a broad MWD of the final product ($\bar{M}_w/\bar{M}_n > 4$).

The degradation of *cis*-polyisoprene in dilute solutions in hydrocarbons proceeds at a considerably lower rate[115]. In view of the high sensitivity of the polymer to cationic reactions, due to the presence of tungsten and alkylaluminium halides, the process is carried out in the presence of an electron donor (anisole, etc.). The $W[OCH(CH_2Cl)_2]_2Cl_4$–$Al(C_2H_5)_2Cl$–anisole metathesis system (with the ratios Al : W : AH=5 : 1 : 5) is extremely stable and remains active for several days. The degradative cyclisation of polyisoprene makes it possible to obtain oligomers with more than 97% of *cis*-units and the theoretical degree of bond unsaturation; $[\eta] = 0.3$, while the initial intrinsic viscosity is $[\eta] = 5.9$ ($\bar{M}_v = 1.07 \times 10^6$).

As already mentioned previously, the degradative cyclisation of polyalkenamers takes place in the polymerisation of cyclo-olefins simultaneously with the chain propagation reaction. It has been shown[113,114] that the decrease of the molecular weight of the polymer during the polymerisation of cyclo-octa-1,5-diene at an initial monomer concentration of 8 wt.% is particularly rapid after the consumption of the monomer. The cyclo-oligomers formed, with $[\eta] = 0.22$, are characterised by a broad MWD ($\bar{M}_w/\bar{M}_n = 4$–5).

It has been established that the concentration of cyclo-oligomers increases with time[116] and that the state of equilibrium depends on the initial concentration of double bonds in the system[114]. The equilibrium concentrations of the cyclo-oligomers of cyclo-octa-1,5-diene and cyclo-octene have been found and their entropies of formation have been determined[117].

Thus the application of metathesis catalysts made it possible to achieve intramolecular cyclisation reactions, which had been previously believed to be characteristic solely of polycondensation processes. Jacobson and Stockmayer[118] were the first to examine theoretically the ring–linear chain equilibrium and pointed out the possibility of obtaining macrocyclic polymers under conditions close to the critical concentration of the solution. Studies of the hydrodynamic properties of solutions of polyoctadienamer relative to linear 1,4-polybutadiene permitted the conclusion that macrorings are present in cyclo-octa-1,5-diene polymers[48]. Scott[154] arrived at an analogous conclusion on the basis of the gel-chromatographic analysis of high-molecular-weight polypentenamer specimens.

2. Degradation of Polyalkenamers in the Presence of Linear Olefins

The cometathesis of polyalkenamers with linear olefins made it possible to achieve a more far reaching degradation process in order to obtain low-molecular-weight linear oligomers.

Low-molecular-weight *cis*-oligomers of isoprene[115] were first obtained by the degradation of high-molecular-weight *cis*-polyisoprene in the presence of the $Cl_4W[OCH(CH_2Cl)_2]_2$–$Al(C_2H_5)_2Cl$–anisole system and linear olefins (Table 6). The formation of oligomers with the most probable molecular weight distribution and a slight loss of unsaturation, due to the presence in the oligomers of residues of C_9–C_{19} olefins in the form of end groups, are characteristic features in this instance.

The products of the degradation of 1,4-polybutadiene in the presence of oct-4-ene and dodec-6-ene under the influence of the WCl_6–$Al(C_2H_5)Cl_2$ catalyst have been investigated chromatographically in a series of studies[119–121] and oligomers having the general formula $R=[=CH-(CH_2)_2-CH=]_n=R$, where R is the residue of a symmetrical olefin and $n = 1$–4, were obtained. A function for the final molecular weight distribution of the linear products of the cometathesis of

polyalkenamers with olefins was obtained[122] and is one of the variants of the statistical Schultz–Flory distribution.

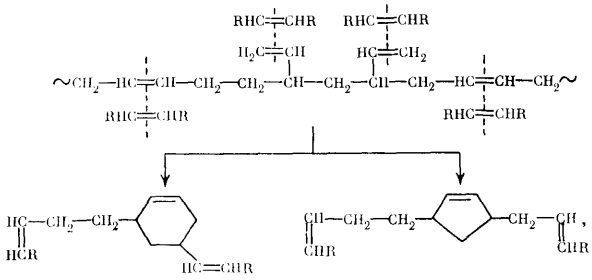
The degradation of modified rubbers[126–128] does not proceed quite so smoothly and the yield of oligomeric products is as a rule low. The cometathesis of partially hydrogenated 1,4-*cis*-polybutadiene (which is a successful model of the ethylene–butadiene copolymer) with oct-4-ene has been carried out in the presence of the WCl_6–$Sn(CH_3)_4$ system[123,124]. Analysis of the composition of the low-molecular-weight products permitted the conclusion that the homogeneous hydrogenation is statistical in character, while in heterogeneous catalytic hydrogenation the formation of block structures was observed.

Table 6. Certain properties of the oligomers obtained by the cometathesis of *cis*-polyisoprene with C_9–C_{12} α-olefins in the presence of the $Cl_4W(OR)_2$–$Al(C_2H_5)_2Cl$–anisole system (Al : W : AH = 5 : 1 : 5, 20 °C).

$[\eta]$*, dl g^{-1}	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Loss of unsaturation a, %	Content of units, %		
					cis-	3,4-	*trans*-
0.15	8390	4160	2.01	6	95	3	2
0.16	11 150	5000	2.23	8	96	3	1
0.12	6 200	3100	2.00	7	94	3	3

*Initial viscosity $[\eta]$ = 5.9.

The degradation of cross-linked rubbers in order to elucidate their structure was investigated by Ast and co-workers[123,125] and Hümmel and co-workers[129,130]. Studies of the degradation of a weakly cross-linked 1,4-*cis*-polybutadiene in the prsence of hex-3-ene have been carried out[130] over a wide range of temperatures and component ratios of the WCl_6–$Al(C_2H_5)Cl_2$ catalytic system in order to discover the optimum process conditions. An interesting result has been obtained in a study[131] where the possibility of obtaining mono- and di-substituted cyclopentenes and cyclohexenes by the cometathesis of polybutadienes having a high content of 1,2-units with various olefins has been demonstrated. The reaction takes place in the presence of the catalytic system WCl_6–$Sn(C_2H_5)_4$–$(C_2H_5)_2O$ via the mechanism



and when hex-3-ene is used, but-1-ene, which is a product of the cometathesis of the vinyl groups with the initial olefin, is also formed[132].

III. THE SYNTHESIS OF POLYMERS AND OLIGOMERS BY THE METATHESIS OF CYCLO-OLEFINS

1. Thermodynamics of Ring Opening in Cyclo-olefins

A characteristic features of the polymerisation reactions of the majority of cyclo-olefins under the influence of metathesis catalysts is low enthalpy changes, which makes it possible to carry out the reaction in solutions at high concentrations and in bulk in the monomer. The heat of reaction depends on the strain energy of the initial cyclo-olefin, which is determined by the distortion of the main valence angles of the carbon–carbon bonds and the deformation resulting from the interaction of the atoms non-bonded by valence forces.

Data allowing inferences about the strain energies of the rings in cyclo-olefins have not yet been obtained for all cyclo-olefins. To a certain extent, the heats of hydrogenation of cyclo-olefins reflect the ring strain. It has been shown, for example, that the heats of hydrogenation of *trans*- and *cis*-cyclo-octenes are 134.8 and 98.1 kJ mol^{-1} respectively[133], which indicates a greater ring strain in the *trans*-isomer. The heat of hydrogenation of bicyclo-[2.2.1]hept-2-ene (norbornene) is extremely high and amounts to 138.4 kJ mol^{-1}.[133]

The ring strain energy of C_5 and C_6 cyclo-olefins should be minimal. As a consequence of the low enthalpies of ring opening, the equilibrium for these monomers is markedly displaced towards the monomer. The ΔH_n, ΔS_n^0, and G_n^0 for the polymerisation processes cyclopentene (liq.) → *trans*-polypentenamer (h.e.†) [134] and cyclopentene (liq.) → *cis*-polypentenamer (h.e.) [135] have been determined in a number of studies and the limiting temperatures of these transitions have been estimated (305 and 350 K respectively[135]).

Table 7. Thermodynamic parameters of the polymerisation of cyclo-olefins in bulk (298.15 K; 101.325 kPa).

Monomer	Physical state of monomer and polymer*	$-\Delta H_n$, kJ mole^{-1}	$-\Delta S_n^0$, J mole^{-1}K^{-1}	$-\Delta G_n^0$, J mole^{-1}	Refs.
Cyclopentene**	—	18.4	62.3	—	[65]
Cyclopentene***	—	15.5	67.7	—	[66]
Cyclopentene	liq.; *cis*-h.e.	15.4	51.8	0.27	[134,135]
Cyclopentene	liq.; *trans*-h.e.	18.1	51.8	2.56	[134,135]
Cyclohexene	liq.; *cis*-h.e.		31.0	—6.2	[136]
Cyclohexene	liq.; *trans*-h.e.	—(1—3)	28.0	—7.2	[136]
4-Methylcyclohexene	liq.; liq.	—1.2	49.0	—15.8	[136]
Cyclo-octene	liq.; cryst.	29.8	51.4	14.5	[137]
Cyclo-octene	liq.; h.e.	13.1	—2.9	14.0	[137]
Cyclo-octa-1,5-diene	liq.; h.e.	36.6	29.4	27.8	[137]

*Abbreviations: liq. = liquid, cryst. = crystalline, and h.e. = highly elastic.

**The value for the cyclopentene → *trans*-polypentenamer transition in polymerisation in solution is quoted.

***The value for the cyclopentene → *cis*-polypentenamer transition in polymerisation in solution is quoted.

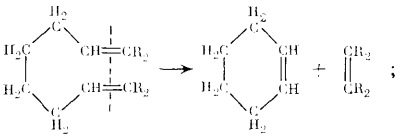
Kulagina[136] and Lebedev[137] determined the thermodynamic parameters of the cyclo-olefin → polyalkenamer transitions for certain other cyclo-olefins: cyclohexene, cyclo-octene,

† Highly elastic (Ed of Translation).

and cyclo-octa-1,5-diene. The enthalpy of polymerisation of the latter monomer has also been determined by Kozina and Cherednichenko[138].

Table 7 presents published standard enthalpies, entropies, and Gibbs free energies for the polymerisation reactions of certain cyclo-olefins. It is seen that the cyclohexene (liq.) → polyhexenamer (h.e.) transition is thermodynamically impossible at room temperature; however, the positive Gibbs free energy $\Delta G_n^0 = +6.2$ kJ mol^{-1} is low and does not rule out in principle the possibility of the opening of the cyclohexene ring by metathesis with formation of a crystalline polymer. The available reports in the literature concerning the attempt at the polymerisation of cyclohexene in the presence of metathesis catalysts show that a polyhexenamer has not yet been obtained.

Treatment of non-conjugated octa-1,7-dienes with metathesis catalysts induces the intramolecular ring closure reaction and leads to the formation of cyclohexene[139-141]:



R = H, D.

It has been shown[142] that this reaction proceeds quantitatively and with a selectivity close to 100%. A non-conjugated cyclic diene, namely cyclohexa-1,4-diene, has been obtained analogously by the metathesis of linoleic and linolenic esters isolated from natural oils[143].

The thermodynamic parameters of the polymerisation of 4-methylcyclohexene with ring opening have been determined[136] and it has been shown that the polymerisation is thermodynamically prohibited in all phase states down to 0 K. Indeed it has been established[160] that the alternating butadiene–propene copolymer is fully degraded to 4-methylcyclohexene under the influence of metathesis catalysts.

The ring strain in cyclo-olefins such as *cis*-cyclo-octene and *cis,cis*-cyclo-octa-1,5-diene (Table 7) is fairly high and the equilibrium monomer concentration is low at the usual temperatures.

2. Synthesis of Cyclo-olefin Polymers and Oligomers

The metathesis reactions of cyclo-olefins make it possible to obtain polymers which could not be synthesised by the methods of polymer chemistry known previously. Among all the cyclo-olefin polymers known at the present time, those of cyclopentene, norbornene, and cyclo-octene have acquired the greatest technical importance.

Polypentenamer, in which the double bonds have predominantly the *trans*-configuration, is obtained by the polymerisation of cyclopentene under the influence of metathesis catalysts based on tungsten compounds, for example WCl_6–$Al(C_2H_5)_3$ [5] and WCl_6–C_2H_5OH–$Al(C_2H_5)Cl_2$ [65] at room temperature. A polymer with a high content of *trans*-units has also been obtained using tungsten hexafluoride in combination with $Al(C_2H_5)Cl_2$.[18] In the polymerisation of cyclopentene in the presence of the WCl_6–$Al(C_2H_5)_3$ system modified by the introduction of benzoyl peroxide, the content of *trans*-units reaches 90%.[144] The melting point of *trans*-polypentenamer (80% of *trans*-units) is close to room temperature; this polymer is capable of undergoing forced crystallisation on extension, which leads to the spontaneous strengthening of rubbers[145,146].

The *cis*-polypentenamer described by Natta et al.[5] was obtained in the presence of the $MoCl_5$–$AlEt_3$ molybdenum-containing catalyst. Later Haas et al.[18] reported the synthesis of a polypentenamer containing up to 85% of *cis*-units, for which tungsten hexafluoride and a polymerisation temperature of −30 °C were employed. An effective system for the catalysis of the *cis*-polymerisation of cyclopentene, proposed by Makovetskii and Red'kina[66], consists of a combination of WCl_6 with tetra-allylsilane and ensures the formation at −30 °C of a polypentenamer containing 98% of *cis*-units. The *cis*-polypentenamer obtained has the lowest glass point $T_g = -114$ °C among polyhydrocarbons and exhibits an extremely low rate of crystallisation at low temperatures (−78 °C).[35,144] This elastomer is one of the most frost-resistant rubbers.

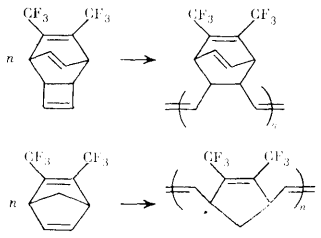
Polynorbornene, the polymer of norbornene, which is the first representative of the group of bicyclo-olefin polymers, has also found a practical application. Oil-filled rubbers (up to 400 wt.%) based on it are manufactured and are used as vibration eliminating materials[85,96]. The polymerisation of this most reactive cyclo-olefin with ring opening can be achieved in the presence of virtually any metathesis catalyst[17,147], including titanium-containing catalytic systems[3]. The polymers obtained, having a mixed *cis/trans* configuration (43/57), have an amorphous structure and $T_g = 54$ °C.[148] A *trans*-polyoctenamer, a crystalline polymer with a melting point of 62 °C and containing 90% of *trans*-units[6], has been obtained by the polymerisation of cyclo-octene in the presence of the WCl_6–$Al(C_2H_5)Cl_2$ system. A polyoctenamer with a melting point of 58 °C and containing 65% of *trans*-units has been obtained in the presence of the WCl_6–$Al(iso\text{-}Bu)_2Cl$ system[150]. This polymer can be of interest for the preparation of biodegradable films. Its *cis*-isomer is also promising as regards practical applications[151]. As a consequence of the relatively low content of α-methylene groups at the double bonds, this elastomer is much more resistant to oxidation than rubbers based on butadiene and isoprene. A disadvantage of *cis*-polyoctenamer is a high rate of crystallisation. However, its capacity for crystallisation can be appreciably reduced by the introduction of *trans*-units. Thus polyoctenamers containing approximately 30% of *trans*-units do not crystallise down to −100 °C.[152]

The polymerisation of cyclo-octa-1,5-diene leads to the possibility of obtaining polymers (analogues of 1,4-polybutadiene) without vinyl side groups; however, the formation of oligomeric products in the course of polymerisation[100,149] renders this process unpromising from the practical standpoint.

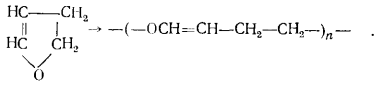
Various rubbers, including non-crystallisable rubbers, can be obtained from cyclo-octa-1,5-diene–cyclo-octene copolymers. These have not undergone a technical development because the above cyclo-olefins are not manufactured in sufficient amounts. The copolymerisation reactions of various cyclo-olefins have been investigated in detail[148,150,153].

The modification of finished rubbers can be achieved by their cometathesis with cyclo-olefins containing functional groups or by the copolymerisation of the usual cyclo-olefins and cyclo-olefins with functional group substituents. Thus the copolymerisation of the *exo*-adduct of cyclopentadiene and maleic anhydride with cyclopentene has been achieved[155] and a polymer containing anhydride groups has been obtained. It is of interest that the *endo*-adduct does not exhibit a catalytic activity in the metathesis reaction.

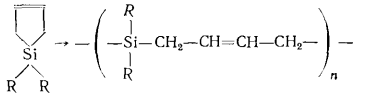
Polymers of fluorine-containing cyclo-olefins have been obtained[156,157]:



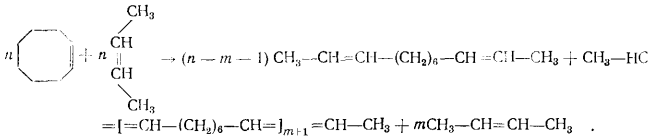
It has been shown[73] that 2,3-dihydrofuran can be polymerised with ring opening in the presence of the stable Fischer carbenechromium complexes $(CO)_5Cr{=}CPh_2$ and $(CO)_5Cr{=}C(OCH_3)Ph$:



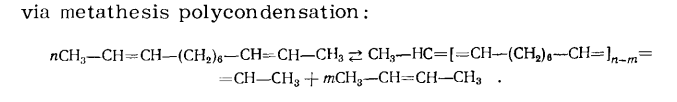
The polymerisation of dialkylsilacyclopentene with ring opening in the presence of metathesis catalysts had been reported even earlier[158]:



The cometathesis of cyclic and linear olefins as well as the degradation reactions of saturated polymers in the presence of linear olefins are reactions of the same type and can be used to synthesise linear unsaturated oligomers. In this case linear olefins are effective chain transferring agents comparable in their reactivity with cyclo-olefins. The cometathesis of cyclopentene and cyclo-octene with *cis*- and *trans*-but-2-enes and *trans*-oct-4-ene under the influence of the WCl_6–tetramethyldisilacyclobutane system in stoichiometric proportions of the olefins has been studied[159]. The cometathesis reaction was completed by the formation of linear oligomers in a quantitative yield. The ratios of the rate constants for reactions involving chain transfer to a linear olefin and the propagation rate constants were 0.16 (cyclo-octene–*trans*-octene), 0.48 (cyclo-octene–*trans*-but-2-ene), and 0.82 (cyclo-octene–*cis*-but-2-ene), which indicates virtually identical reactivities for *cis*-but-2-ene and cyclo-octene. In the latter case mainly the linear dodeca-2,10-diene and a small amount of oligomers are formed for equimolar amounts of cyclo-octene and *cis*-but-2-ene:[115]



The removal of the equilibrium amount of but-2-ene leads to an increase of the molecular weight of linear oligomers via metathesis polycondensation:



This reaction proceeds via stages with a chain mechanism and at the same time has the main features of equilibrium polycondensation. The determination of the equilibrium constant yielded a very low value (1.3×10^{-3}), which indicates an almost complete shift of the equilibrium to the left. Nevertheless, if the low-molecular product (but-2-ene) is carefully removed from the reaction mass, it is possible to obtain oligomers with $\bar{M}_n = 20\,000$.

The synthesis of oligomers of cyclo-octa-1,5-diene and cyclo-octene by their cometathesis with oct-1-ene, propene, pent-1-ene, hex-1-ene, and hept-1-ene has been described[152]. The use of higher C_9–C_{12} α-olefins makes it possible to regulate simultaneously the degree of unsaturation of the oligomers obtained. Thus products whose degree of unsaturation was close to that of plant oils have been obtained in this way from cyclopentene[160].

The cometathesis reactions of polybutadiene and polyisoprene with olefins are undoubtedly of interest as a new method for the synthesis of oligomeric products. The process takes place at room temperature and leads to the formation of low-molecular-weight isoprene *cis*-oligomers and butadiene oligomers with a mixed structure. In contrast to the degradative cyclisation process, in the latter case oligomeric products are characterised by an exponential equilibrium distribution ($\bar{M}_w/\bar{M}_n \cong 2$).[115] The use of metathesis catalysts also leads to the possibility of carrying out the degradation of polybutadiene and polyisoprene gels with transfer of the degradation products to the solution.

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Thus it was shown above that the metathesis reaction proceeds via a chain mechanism under the influence of carbene complexes of transition metals. The carbene species are formed on decomposition of organometallic compounds of transition metals at the instant of their generation. In the presence of metathesis catalysts degradative chain cyclisation of unsaturated polymers takes place at room temperature with formation of a set of cyclic oligomeric molecules having a broad molecular weight distribution. In the presence of olefins the same reactions lead to linear oligomers with the most probable molecular weight distribution. The metathesis reaction is promising from the standpoint of the synthesis of polymeric materials.

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Institute of Petrochemical Synthesis,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 87-106 (1984) U.D.C. 541.64:547.241

Polyfluoroalkoxyphosphazenes—a Promising Class of Organoelemental Polymers

S.V.Vinogradova, D.R.Tur, and I.I.Minosyants

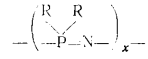
The results of the synthesis of polyfluoroalkoxyphosphazenes and also polyorganophosphazenes containing various non-fluorinated organic groups as substituents at the phosphorus atoms together with fluoroalkoxy-groups are surveyed. The characteristics of the formation of these polymers by the chemical modification of polydichlorophosphazene are examined. A systematic account is given of the literature data on the properties of polyfluoroalkoxyphosphazenes and their practical applications. The ways in which varieties of the macromolecules of these polymers arise and the influence of the nature and number of anomalous units on their properties are considered. Attention is drawn to a fundamentally important characteristic feature of polyfluoroalkoxyphosphazenes, namely the high sensitivity of their properties to anomalous units when the content of the latter is less than 1 mole %.
The bibliography includes 179 references.

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I. INTRODUCTION

Among high-molecular-weight polyorganophosphazenes having the general structure



most attention has been attracted at the present time by polyfluoroalkoxyphosphazenes, where R = $OAlk_F$, which have properties of interest from the practical point of view. The chemical structure of their macromolecules has the following features. The main chain is made up of alternating phosphorus and nitrogen atoms and each second chain atom (nitrogen) has no substituents. Furthermore, the presence of fluoroalkoxy-groups as substituents at the phosphorus atom is responsible for a comparatively high fluorine content in these polymers (more than 40%). This ensures the following properties of polyfluoroalkoxyphosphazenes: flexibility and elasticity at low temperatures, effective resistance to oil and petrol, improved fire resistance, water- and dirt-repelling properties, etc.

During the last ten years, a comparatively large number of studies have been published on polyfluoroalkoxyphosphazenes, demonstrating the undoubted interest of investigators in these polymers. At the same time a series of the existing reviews[1-26] and monographs[27-34] deal with polyfluoroalkoxyphosphazenes either together with other polyphosphazenes, merely as one of the possible types of such polymers, or in terms of a specific aspect of their properties, so that the treatment is incomplete and insufficiently comprehensive.

This review surveys the main literature data on the synthesis, properties, and the most promising applications of polyfluoroalkoxyphosphazenes.

II. THE SYNTHESIS OF POLYFLUOROALKOXYPHOSPHAZENES

Polyfluoroalkoxyphosphazenes are comparatively new polymers. The first data concerning their successful synthesis were published almost simultaneously in the Soviet Union[35] and in the USA [36,37] as late as 1965–1966, when comparatively high degrees of nucleophilic substitution of the chlorine atoms in a high-molecular-weight fully soluble polydichlorophosphazene by fluoroalkoxy-groups were achieved and polyorganophosphazenes with an improved hydrolytic stability were obtained.

Later, attempts were made to synthesise polyfluoroalkoxyphosphazenes also by other procedures. Thus, Prons et al.[38] tried to carry out the thermal polymerisation of hexakis(3,3,3,2,2-pentafluoropropoxy)cyclotriphosphazene and Allcock et al.[39] attempted the synthesis of hexakis(trifluoroethoxy)cyclotriphosphazene in the melt at temperatures in the range 200–300 °C by analogy with the polymerisation of hexachlorotriphosphazene[36,37] However, it was found that fully substituted fluoroalkoxycyclotriphosphazene cannot be subjected to thermal polymerisation. On the other hand, it has been shown that rings with different degrees of substitution of the chlorine atoms nevertheless enter into both polymerisation and copolymerisation reactions[38] but with formation of a polymer having a lower molecular weight {the intrinsic viscosity $[\eta] = 0.5 - 0.6$ dl g^{-1} in organofluorine solvents} than in the polymerisation of hexachlorocyclotriphosphazene. The copolymerisation of partly substituted cyclic compounds with hexachlorocyclotriphosphazene[39] followed by the substitution of the residual chlorine by trifluoroethoxy-groups yielded polyorganophosphazenes with a much higher molecular weight (100000–400000). A polyphosphazene with a molecular weight of 110000 and $[\eta] = 0.71$ dl g^{-1} has been obtained in solution in tetrahydrofuran by Allcock et al.[39] and in the copolymerisation of hexakis(trifluoroethoxy)cyclotriphosphazene and hexachlorotriphosphazene.

Despite the fact that the above studies led to the discovery of the possibility, in principle, of the polymerisation of partly substituted cyclic compounds, this method of synthesis of polyfluoroalkoxyphosphazenes is of theoretical rather than practical interest owing to its more laborious nature and lower molecular weights of the resulting polymers than in the case where polydichlorophosphazene is used as the starting material.

Together with the attempt at the thermal polymerisation of fluoroalkoxycyclotriphosphazenes, studies have also been made of the possibility of their catalytic polymerisation[39,40].

However, the formation of a high-molecular-weight poly-[bis(trifluoroethoxy)phosphazene] from hexakis(trifluoroethoxy)cyclotriphosphazene in the presence of CsCl as the catalyst at 275 °C was not observed[39].

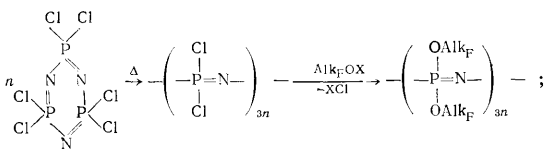
Kolkmann[40] studied the possibility of the polymerisation of hexakis(trifluoroethoxy)cyclotriphosphazene in the presence of acid catalysts such as BCl_3 (at 150 °C), BF_3, BBr_3, $TiCl_4$ (at 120–200 °C), CF_3SO_3H, $CF_3Se(O)OH$, and HCl, as well as basic catalysts such as K_2CO_3, Li_2O, MgO, CaO, BaO, CoO, and $N(C_2H_5)_3$, and also water (at 150 °C). The formation of a polyphosphazene with a molecular weight of 23000–33000, in which approximately half of the initial fluoroalkoxy-groups have been exchanged for chlorine, was observed only in the presence of an equimolar amount of BCl_3. Hexakis(hexafluoroisopropoxy)cyclotriphosphazene does not polymerise and does not react with BCl_3 at 225 °C according to Kolkmann's data[40].

Thus investigators have still not been able to find a realistic method for the polymerisation of fully substituted cyclic compounds—hexa(fluoroalkoxy)cyclotriphosphazenes.

Flindt and Rose[41] showed that poly[bis(trifluoroethoxy)-phosphazene] with a molecular weight of 10000 and soluble in acetone, isobutyl methyl ketone, tetrahydrofuran (THF), and ethyl acetate is formed from tris(1,1,1-trifluoroethoxy)-*N*-trimethylsilylphosphine imine at 200 °C.

Yet another procedure for the synthesis of linear oligomeric fluoroalkoxyphosphazenes from hexachlorocyclotriphosphazene and organosilanes having the formula $ROSiMe_3$, where R = $HCF_2CF_2CH_2$ or $HCF_2(CF_2)_3CH_2$, in the presence of a mixture of H_3PO_4 and pyridine and also polyphosphoric acid as catalysts, has been proposed[42–44].

Among the methods of synthesis of high-molecular-weight polyfluoroalkoxyphosphazenes known at the present time, the most promising is a two-stage procedure consisting of the thermal polymerisation of hexachlorocyclotriphosphazene with formation of polydichlorophosphazene and subsequent substitution of the chlorine atoms in the latter by fluoroalkoxy-groups in accordance with the mechanism



X = H, metal.

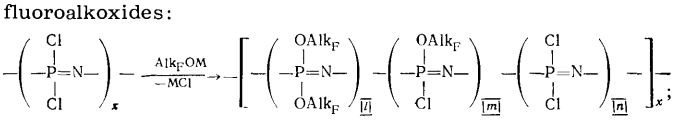
Before proceeding to a deeper analysis of the literature data on the synthesis of polyfluoroalkoxyphosphazenes by this method, it is useful to consider briefly the intermediate product—polydichlorophosphazene. In the early studies devoted to the polymerisation of hexachlorocyclotriphosphazene and considered in fair detail in a number of reviews[45–48], a cross-linked insoluble polydichlorophosphazene, virtually unsuitable for further reactions involving the substitution of chlorine by fluoro-alkoxy-groups, was mainly obtained. It was not until 1965–1966 that a fully soluble polydichlorophosphazene was obtained for the first time[35–37] and it was shown that the cross-linked polymer is not a direct polymerisation product but is formed from a non-cross-linked polymer[36]. It was also shown that a fully soluble polydichlorophosphazene can be obtained at a rigorously controlled temperature (250° ± 1 °C) by stopping the heating of the system when the polymerisation mixture loses its fluidity[28].

There is still no unanimous view among investigators concerning the chemical structure of the soluble polydichlorophosphazene. For example, Singler et al.[80] attribute a linear structure to the polymer, while Allcock[28] believes that the soluble polydichlorophosphazene obtained by the polymerisation of hexachlorocyclotriphosphazene by limiting the degree of conversion has almost certainly a branched structure. However, in both cases these are merely assumptions by the investigators, because polydichlorophosphazene was in no way characterised from this standpoint in their studies.

The influence of the heterounit structure of the initial polydichlorophosphazene, due to the branching of its macromolecules, on the synthesis and properties of polyorganophosphazenes was studied for the first time by Korshak et al.[49] It was shown experimentally in relation to the polymer-analogue substitution of chlorine atoms in the linear[50,51] and branched[52] polydichlorophosphazenes by trifluoroethoxy-groups that the presence of branches hinders the attainment of high degrees of substitution and has a significant influence on the solubility and thermomechanical properties of the polyorganophosphazene formed[49].

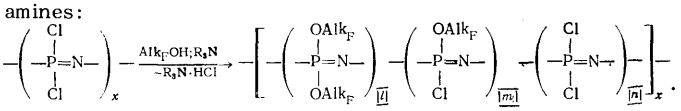
These data permit the conclusion that, in order to obtain reliable, satisfactorily reproducible results in the synthesis of polyfluoroalkoxyphosphazenes, it is necessary in the first place to characterise rigorously the initial polydichlorophosphazene not only in terms of the molecular weight but also in terms of the degree of branching.

The substitution of chlorine atoms in polydichlorophosphazene by fluoroalkoxy-groups in a series of organic solvents has been achieved in two ways—by condensation with fluoroalkoxides:



M=Na, Li, K; $l \gg m + n$

and with fluorinated alcohols in the presence of tertiary amines:



The characteristics of these reactions have still been little studied and most of the literature data on the synthesis of polyfluoroalkoxyphosphazenes reduce mainly to the description of methods for the preparation of specific specimens of such polymers.

Thus the synthesis of these polymers using sodium fluoroalkoxides as the nucleophiles has been described in a number of studies[36,37,53–67]. Some investigators used lithium[34,60,64,65] and potassium[65,70] fluoroalkoxides together with sodium fluoroalkoxides for the same purpose.

Unfortunately, analysis of the literature data does not permit a conclusion about the advantages of a particular alkali metal in the given polymer–analogue substitution reactions and systematic studies on these lines have not been carried out. At the same time, sodium fluoroalkoxides are used most often apparently mainly because sodium is most readily available and is easiest to handle.

According to Sharov and co-workers[60,65], the nature of the alkali metal can, however, influence the stage of aggregation of the fluoroalkoxyphosphazene polymers. In particular, under comparatively mild conditions of synthesis, when the polarity of the reaction medium (diethyl ether–toluene or dibutyl ether–toluene) is low and at reaction temperatures not exceeding 60 °C, amorphous polymers are formed when lithium fluoroalkoxide are used. The polymers obtained under the same conditions but using sodium and potassium fluoroalkoxides have a crystalline structure.

In the synthesis of polyfluoroalkoxyphosphazenes based on the macromolecular reaction of polydichlorophosphazene with sodium fluoroalkoxides, benzene[37,53–59,65,67], toluene[55–67],

chlorobenzene[55,57], and THF [57,61,62,67] were used as solvents for polydichlorophosphazene. Sodium fluoroalkoxides were obtained in solution in THF,[37,53-67] dioxane[55,67], diethyl ether[65], dibutyl ether[65], and diethylene glycol dimethyl ether[55]. In the course of the substitution of the chlorine atoms in polydichlorophosphazene by fluoroalkoxy-groups using sodium fluoroalkoxides, the polyorganophosphazenes formed are as a rule precipitated[37,53-60,65-67]. It has been suggested in the patent literature[61,62] that, in order to improve the rate of reaction and the degree of substitution of chlorine atoms by fluoroalkoxy-groups, the substitution reactions be carried out under homogeneous conditions in THF, in which certain polyfluoroalkoxyphosphazenes are readily soluble. The amount of unsubstituted chlorine in these compounds amounts to 0.06 wt.% under these conditions according to patent data[61,62]. Allcock and Cook[57] also obtained poly[bis(2,2,3,3-tetrafluoropropoxy)phosphazene] in solution in tetrahydrofuran but with a much higher content of unsubstituted chlorine (0.42 wt.%). At the same time, despite the precipitation of the polymer, a series of polyfluoroalkoxyphosphazenes whose chlorine content did not exceed 0.05 wt.% were successfully synthesised in mixtures of solvents such as benzene and THF.[56,59] Hence it is evident that the "homogeneity" or "heterogeneity" of the reaction mass is not always a decisive factor for the attainment of high degrees of the substitution reaction.

Among investigators there is no unanimous view concerning the optimum temperature for the successful polymer-analogue substitution of chlorine by fluoroalkoxy-groups. This reaction has been carried out most frequently by prolonged refluxing of the reaction mixtures[36,37,53,55,57,58,61,62] but in certain studies lower temperatures, for example 40 °C, have also been indicated[56,59].

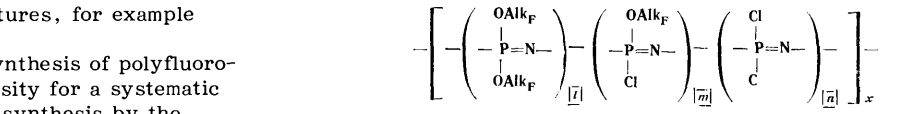
This state of the problem of the synthesis of polyfluoroalkoxyphosphazenes led to the necessity for a systematic study of the characteristics of their synthesis by the chemical modification of polydichlorophosphazene with fluoroalkoxides. In relation to the synthesis of poly[bis(trifluoroethoxy)phosphazene], we investigated the influence of various factors on the degree of the polymer-analogue substitution of chlorine atoms in polydichlorophosphazene by fluoroalkoxy-groups[67,69] and on the effectiveness of the hydrolytic side reactions during synthesis[66-68].

The investigation established that the main polymer-analogue reaction involving the substitution of chlorine by trifluoroethoxy-groups with the aid of sodium trifluoroethoxide is as a rule characterised by high degrees of conversion even in those cases where the polyfluoroalkoxyphosphazene does not dissolve in the reaction medium and precipitates after only a few minutes from the start of the reaction. On the other hand, the absolute amounts of the residual chlorine then depend on the temperature, the nature of the solvents, and the concentrations and ratios of the initial component. The highest degrees of the substitution reaction (up to 99.95 mole %) are obtained in solvent mixtures such as benzene–THF, toluene–THF or in solution in THF at room temperature for a reaction time of ~3 h, a concentration of the initial polydichlorophosphazene of ~20 g l^{-1}, and in the presence of a threefold excess of sodium trifluoroethoxide calculated per P–Cl group. The effectiveness of hydrolytic side reactions is determined by the nature of the solvent, the temperature, and the duration of the substitution reaction and depends significantly on the amount of water in the reaction system (even at the level of 10^{-2}–10^{-3} vol.%). Hydrolytic side reactions take place to the least extent at room temperature when the main reaction time is not more than 3 h and polyfluoroalkoxyphosphazene precipitates during the reaction, particularly from a toluene–THF mixture.

Since the unsubstituted P–Cl groups in polyphosphazenes are hydrolytically extremely unstable[28], the attainment of high degrees of the substitution reaction is naturally urgently required in the synthesis of polyfluoroalkoxyphosphazenes. Because of this, the degree of substitution is one of the most important characteristics of polymers of this kind. It can be inferred quantitatively from the content of unsubstituted chlorine.

Table 1 lists the contents of unsubstituted chlorine in polyfluoroalkoxyphosphazenes obtained by substituting the chlorine in polydichlorophosphazene by sodium, lithium, and potassium fluoroalkoxides under different substitution reaction conditions. It is seen that the authors of the relevant investigations did not always indicate the amount of unsubstituted chlorine in the polymer. Furthermore, in a number of instances, it was estimated extremely approximately and some workers[36,53,71] actually quote a zero chlorine content, which is unlikely, since polymer-analogue reactions do not as a rule take place to the extent of 100%. Overall, the polyfluoroalkoxyphosphazenes synthesised are usually characterised by a low content of residual chlorine by weight, which indicates a high degree of the given polymer-analogue substitution reaction.

Table 1. The polyfluoroalkoxyphosphazenes

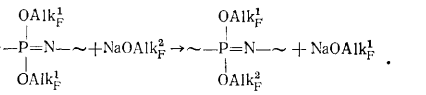


obtained by substituting the chlorine in polydichlorophosphazene by fluoroalkoxides.

Alk_F	Cl content, wt.%	Refs.
CF_3CH_2	Not detected	[36]
CF_3CH_2	0	[53,71]
CF_3CH_2	0.03	[56,59]
CF_3CH_2	0.057	[67]
CF_3CH_2	0.11	[57]
CF_3CH_2	<0.10	[60,65]
CF_3CH_2	<0.06	[62]
CF_3CH_2	Not quoted	[54,58,72–75]
$CF_3CF_2CH_2$	Not quoted	[2,42,28,35]
$CF_3(CF_2)_2CH_2$	0.05	[56,59]
$CF_3(CF_2)_2CH_2$	Not quoted	[28,35,55]
$CF_3(CF_2)_3CH_2$	<0.10	[60,65]
$CF_3(CF_2)_5CH_2$	Not quoted	[35]
$CF_3(CF_2)_6CH_2$	Not quoted	[54,72]
$HCF_2CF_2CH_2$	0.42	[57]
$HCF_2CF_2CH_2$	<0.10	[60,65]
$HCF_2CF_2CH_2$	Not quoted	[2,9,28]
$HCF_2(CF_2)_3CH_2$	0.03	[60,65]
$HCF_2(CF_2)_3CH_2$	<0.10	[60,65]
$HCF_2(CF_2)_5CH_2$	<0.10	[60,65]
$CF_3O(CF_2)_2CH_2$	Not quoted	[35]
$CF_3CHFCF_2CH_2$	0.10	[70]

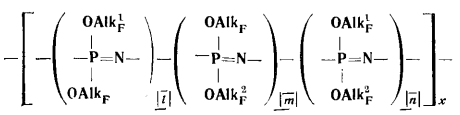
A large number of polyfluoroalkoxyphosphazenes containing various fluoroalkoxy-groups as substituents at the phosphorus atoms have now been obtained. These are, firstly, polyfluoroalkoxyphosphazenes in the synthesis of which mixtures of two different fluoroalkoxides were used for the reaction with polydichlorophosphazene[56,59,76-87] (Table 2). At the same time, the synthesis of polyfluoroalkoxyphosphazenes by the substituent exchange reaction

on heating in solution, in accordance with the following scheme, has been described[88,89]:



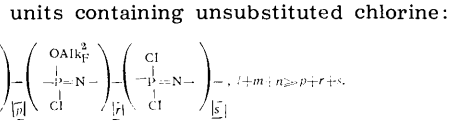
Using dihydric fluorinated alcohols, for example, 2,2,3,3,4,4-hexafluoropentanediol, the vulcanisation of polyfluoroalkoxyphosphazenes can be achieved by this reaction[89,90].

Table 2. Polyfluoroalkoxyphosphazenes with two different fluoroalkoxy-groups as substituents at the phosphorus atoms*.



Alk_F^1	Content, moles	Alk_F^2	Content, moles	Refs.
CF_3CH_2	1	$CF_3(CF_2)_2CH_2$	1	[56,59,76—81]
Ditto	1	ditto	3	[77]
»	2	»	1	[80]
»	3	»	1	[77]
CF_3CH_2	1	$CF_3(CF_2)_3CH_2$	1	[77]
CF_3CH_2	1	$HCF_2(CF_2)_2CH_2$	1	[82]
CF_3CH_2	1	$HCF_2(CF_2)_3CH_2$	1	[56,59,79,81, 83,84]
Ditto	0.64	ditto	0.36	[85,86]
»	0.65	»	0.35	[87]
CF_3CH_2	1	$CF_3CHFCF_2CH_2$	1	[70]
Ditto	1	ditto	3	[70]
»	3	»	1	[70]
$CF_3CF_2CH_2$	1	$CF_3(CF_2)_2CH_2$	1	[2,12]
$CF_3CF_2CH_2$	1	$CF_3(CF_2)_4CH_2$	1	[77]
$CF_3(CF_2)_2CH_2$	1	$CF_3(CF_2)_6CH_2$	1	[80]
$HCF_2CF_2CH_2$	1	$HCF_2(CF_2)_3CH_2$	1	[77]
$HCF_2CF_2CH_2$	1	$HCF_2(CF_2)_5CH_2$	1	[77,79,81]

*In reality the chemical structure of the copolymers is much more complex owing to the presence of a certain amount of anomalous units containing unsubstituted chlorine:



However, in most cases, the vulcanisable fluoroalkoxyphosphazene polymers contain a small amount of a third substituent at the phosphorus atoms with a reactive group which cross-links the polymer in subsequent chemical reactions, for example, double bonds, active HO and NH groups, silicon-containing groups, and other groups[91—98]. Secondly, polyphosphazenes containing comparable amounts of fluoroalkoxy- and non-fluorinated alkoxy or aryloxy-groups as a framework for the phosphorus atoms can be assigned to the same type.

Among polymers of this kind, a polyorganophosphazene with two different alkoxy-groups at the phosphorus atom, containing 1.6 moles of trifluoroethoxy-groups and 0.4 of a mole of ethoxy-groups[73,74], as well as polyphosphazenes with three different substituents, where the content of alkoxy-groups having less than 16 carbon atoms is up to 35 mole %,[99] have been described. Polyphosphazenes of the type indicated, with reactive hydroxy-groups in the alkoxy-substituents, which are capable of being hardened by reaction with di-isocyanates and tetracarboxylic acid dianhydrides, have been synthesised[100].

In the synthesis of polyphosphazenes with fluoroalkoxy- and aryloxy-groups, various investigators used sodium[101,102] or lithium[103—109] fluoroalkoxides and phenoxides. On the other hand, when polydichlorophosphazene was treated with 4-cyanophenol, Na_2CO_3 was used as the HCl acceptor, after which the partially substituted polyphosphazene was condensed with sodium trifluoroethoxide[110].

In a number of instances, where it was not possible to achieve high degrees of substitution of polydichlorophosphazene with the aid of various nucleophiles, further substitution was carried out very successfully with the aid of sodium trifluoroethoxide[111—119] and lithium 2,2,3,3-tetrafluoropropoxide[109,120,121]. Polymers containing ~50% of fluoroalkoxy-groups as substituents at the phosphorus atom were as a rule obtained under these conditions.

Allcock and co-workers[122—124] obtained coloured polyfluoroalkoxyphosphazenes by substituting some of the chlorine atoms in polydichlorophosphazene by chromophoric groups and the remaining chlorine atoms by trifluoroethoxy-groups. They used the sodium derivatives of 2-hydroxy-1-azonaphthalene, 4-phenylazoaniline, 2-amino-1-phenylnaphthalene, 1-phenylazo-4-*p*-hydroxyphenylazonaphthalene, etc. as the chromophoric reagents, the molar ratio of the usual and chromophoric substituents ranging from 1:1 to 15000:1.

Together with polydichlorophosphazene, Allcock and co-workers[125—127] also used polydifluorophosphazene as the starting material in the synthesis of polymers containing fluorinated and non-fluorinated groups at the phosphorus atom. In particular, the high reactivity of polydifluorophosphazene compared with polydichlorophosphazene made it possible to achieve a degree of substitution of 50—90% of fluorine atoms by alkyl and phenyl groups, while in polydichlorophosphazene phenyl-lithium substitutes only 10% of the chlorine[114]. The residual chlorine atoms were substituted in both cases by sodium trifluoroethoxide. However, studies with polydifluorophosphazene involve considerable experimental difficulties, because of its high sensitivity to hydrolytic side reactions.

As already mentioned above, several attempts to achieve the substitution of chlorine atoms in polydichlorophosphazene by fluoroalkoxy-groups by condensation with fluoroalcohols in the presence of tertiary amines have been described. Thus, as early as 1964, Lenton et al.[128] reported the synthesis of a cross-linked partly substituted polymer by treating dichlorophosphazene swollen in benzene with a mixture of trifluoroethanol and pyridine. According to patent data[53], a soluble polyfluoroalkoxyphosphazene containing ~2% of unsubstituted chlorine can be obtained from the insoluble polydichlorophosphazene by treating it with a mixture of trifluoroethanol and triethylamine.

It is noteworthy that despite the much smaller number of publications on the synthesis of polyfluoroalkoxyphosphazenes in the presence of tertiary amines, a series of important features of this process have already been discovered. In particular, a study has been made of the macromolecular reaction of polydichlorophosphazene with trifluoroethanol in the presence of triethylamine in tetrahydrofuran in the temperature range between −5° and 60 °C.[129,130] It was shown that, together with the substitution of chlorine atoms by trifluoroethoxy-groups, there is a side reaction in this instance between polydichlorophosphazene and triethylamine, leading to the formation of a heterounit polymer containing at best ~3% of unsubstituted chlorine.

Tate et al.[131] synthesised polyorganophosphazenes by substituting the chlorine in polydichlorophosphazene by trifluoroethanol and other non-fluorinated nucleophiles in the presence of triethylamine in THF at 80—120 °C. They

reported that fully substituted non-cross-linked polymers were obtained under these conditions. On the basis of these results, the authors concluded that in the early syntheses the side reactions accompanied by the cross-linking of the polyorganophosphazene were due to the presence of traces of moisture in the reaction medium and the incomplete substitution of chlorine atoms was caused by the short reaction time and mild reaction conditions.

This method of synthesis of polyorganophosphazenes was also used to obtain a large number of polyphosphazenes containing trifluoroethoxy- and various non-fluorinated groups at the phosphorus atom[132-147]. However, according to patent data, such polymers contain 2 wt.%[133] and more[138-140,146] of unsubstituted chlorine, which conflicts to a large extent with the report that the chlorine is fully substituted in the presence of triethylamine[131].

In the presence of triethylamine, other workers[148] obtained in addition phosphazene polymers containing substituents based on thienyl alcohols and trifluoroethoxy-groups at the phosphorus atoms.

Overall, the available literature data on the synthesis of polyfluoroalkoxyphosphazenes in the presence of tertiary amines show that the degree of this reaction is much lower than in the condensation of polydichlorophosphazene with fluoroalkoxides; on the other hand, it greatly exceeds 50% and the attainment of its limiting degree at the level of 90–95% cannot be explained either by a decrease of the reactivity of the second chlorine atom after the substitution of the first or by the increase of steric hindrance. We believe[130] that one can postulate that the effect is due to the properties of the macromolecules in solution, in particular the formation of associated species comprising partly substituted polyphosphazene macromolecules owing to the lower rate of substitution reactions in the presence of tertiary amines compared with alkoxides.

In order to elucidate the possibilities for the synthesis of graft copolymers on the basis of polyphosphazenes, polydichlorophosphazene was condensed with a high-molecular-weight poly(arylene sulphoxide), containing a reactive terminal hydroxy-group, in solution in THF in the presence of triethylamine with subsequent substitution of the chlorine atoms in the polyphosphazene fragments by fluoroalkoxy-groups with the aid of sodium fluoroalkoxides[149] or trifluoroethanol in the presence of triethylamine[150]. The graft copolymers thus obtained contain a comparatively large number of unsubstituted chlorine (2–3 wt.%) like the homofluoroalkoxyphosphazenes synthesised in the presence of tertiary amines.

The above survey of literature data on the synthesis of polyfluoroalkoxyphosphazenes shows that a comparatively large number of polyfluoroalkoxyphosphazenes and polyphosphazenes with various substituents, including fluoroalkoxy-groups, at the phosphorus atoms have already been synthesised. However, the majority of the data are presented in patents and the aim of the relevant studies was to obtain new polyphosphazene structures. The characteristics of the formation of these polymers have been studied mainly only for poly[bis(trifluoroethoxy)phosphazene]. This makes it difficult to survey the literature data in order to discover the general principles of the synthesis of polyfluoroalkoxyphosphazenes.

Nevertheless, detailed examination of specific experimental data obtained by various investigators permits the conclusion that the chlorine atoms in the fully soluble polydichlorophosphazene undergo most successful polymer-analogue substitution by fluoroalkoxides, in the first place sodium fluoroalkoxides. This method of synthesis actually ensures the formation of polyfluoroalkoxyphosphazenes having the highest molecular weights and with a comparatively high degree of substitution.

III. THE PROPERTIES AND APPLICATIONS OF POLYFLUOROALKOXYPHOSPHAZENES

Despite the fact that there are many obscure questions concerning the synthesis of polyfluoroalkoxyphosphazenes, requiring further study, a number of specific and extremely valuable, from the practical point of view, properties of these polymers have already been discovered. The available literature data on the properties of polyfluoroalkoxyphosphazenes mainly refer to polymers with identical or two different fluoroalkoxy-groups at the phosphorus atoms. The properties of polymers with fluorinated and non-fluorinated substituents have so far been very little studied. The literature data only for the properties of polyphosphazenes with fluoroalkoxy-groups will therefore be considered below.

According to the literature, polyfluoroalkoxyphosphazenes can have a partly crystalline or amorphous structure. Thus the polyfluoroalkoxyphosphazenes synthesised by the substitution of the chlorine atoms in polydichlorophosphazene with the aid of sodium fluoroalkoxides have as a rule a partly crystalline structure. This is indicated in particular by X-ray diffraction data for five fluoroalkoxy-substituted polyphosphazenes: $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2C_2F_4H)_2]_n$, $[NP(OCH_2C_2F_5)_2]_n$, $[NP(OCH_2C_3F_7)_2]_n$, and $[NP(OCHC_2F_6)_2]_n$.[28,30] At the same time it has been stated in the literature that fully amorphous polymers are formed under comparatively mild conditions of synthesis when lithium fluoroalkoxides are used[65]. Amorphous poly-[bis(trifluoroethoxy)phosphazene] has been obtained also in the polymer-analogue conversion of polydichlorophosphazene in the presence of triethylamine and LiCl.[49]

Table 3. The solubility of fluoroalkoxyphosphazene polymers.

No.	Polymer	Solvents	Refs.
1	$[NP(OCH_2CF_3)_2]_n$	Acetone, THF, ethyl methyl ketone, cyclohexanone, dimethylformamide	[8,36,37]
2	$[NP(OCH_2CF_2CF_3)_2]_n$	Ethyl trifluoroacetate	[2,28]
3	$\{NP[OCH_2(CF_2)_2CF_3]_2\}_n$	Freon TA*, Freon E-1	[28,59]
4	$\{NP[OCH_2(CF_2)_6CF_3]_2\}_n$	Solvent not found	[54]
5	$[NP(OCH_2CF_2CF_2H)_2]_n$	Acetone, tetrahydrofuran	[2,28]
6	$\{NP[OCH_2(CF_2)_3CF_2H]_2\}_n$	Acetone	[59]
7	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	Freon E-2***	[28,59,76]
8	$\{NP[OCH_2CF_3][OCH_2(CF_2)CF_2H]\}_n$	Acetone	[59,79]
9	$\{NP[OCH_2CF_3]_{0.64}[OCH_2(CF_2)_3 \cdot CF_2H]_{0.36}\}_n$	Isobutyl methyl ketone, THF, ethyl methyl ketone, dimethylformamide, acetone, acetonitrile, dimethyl-acetamide, *N*-methylpyrrolidinone	[85]
10	$\{NP[OCH_2(CF_2)_2CF_3][OCH_2(CF_2)_6 \cdot CF_3]\}_n$	Freon E-2	[80]
11	$\{NP[OCH_2CF_2CF_2H][OCH_2(CF_2)_5 \cdot CF_2H]\}_n$	Acetone	[79]

*Freon TA = azotropic mixture of 1,2,2-trichloro-1,1,3-trifluoroethane and acetone.

**Freon E-1 = $F(CFCF_3CF_2O)CHFCF_3$.

***Freon E-2 = $F(CFCF_3CF_2O)_2CHFCF_3$.

The amorphous or partly crystalline structures of the polymers obtained using a mixture of sodium fluoroalkoxides depend on the chemical structure and proportions of the latter[77]. Depending on their chemical and geometrical structures, these fluoroalkoxyphosphazene polymers are soft plastics or elastomers[28,65,77,81].

Table 3 shows that certain fluoroalkoxyphosphazenes are easily soluble in readily available organic solvents such as acetone, THF, ethyl methyl ketone, etc. However, with increase of the number of CF_2 groups in the side substituents, the solubility of the polymers is significantly impaired. The replacement of the terminal CF_3 group by CF_2H in such substituents again ensures a high solubility of the polymers.

At the same time polyfluoroalkoxyphosphazenes are exceptionally resistant to liquid hydrocarbons[87]. They do not dissolve in hexane and benzene and are fairly resistant to the action of rocket fuel[151], which makes these polymers extremely promising for use as oil- and petrol-resistant rubbers.

The ready solubility of poly[bis(trifluoroethoxy)phosphazene] and also certain polymers with two different fluoroalkoxy-groups at the phosphorus atoms leads to the possibility of the study in greater depth of the hydrodynamic and rheological properties of the solutions and molecular weight characteristics of these polymers. A series of investigations devoted to these questions have already been published[31,78,80,85,152–155]. Table 4 presents the literature data for the molecular weight characteristics of polyfluoroalkoxy-phosphazenes. It is seen that all the test specimens are characterised by a very high molecular weight and a broad molecular weight distribution.

Table 4. Molecular weight characteristics of certain polyfluoroalkoxyphosphazenes.

No.	Polymer	$[\eta]$, dl g^{-1}	$10^{-6}\bar{M}_w$	$10^{-6}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Refs.
1	$[NP(OCH_2CF_3)_2]_n$	1.27*	1.5	—	—	[31]
2	$\{NP[OCH_2CF_3]_{0.65}[OCH_2(CF_2)_3CF_2H]_{0.35}\}_n$	1.9*	8.2	26.7	30.6	[85]
3	$\{NP[OCH_2CF_3][OCH_2(CF_2)_3CF_2H]\}_n$	2.1*	—	—	6.8	[153]
4	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	0.96**	3.1	11.7	26.5	[80]
5	$\{NP[OCH_2CF_3][OCH_2(CF_2)_3CF_3]\}_n$	1.06**	13.0	16.4	79.2	[80]
6	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	1.47**	10.00	15.8	63.2	[80]
7	$\{NP[OCH_2CF_3][OCH_2(CF_2)_2CF_3]\}_n$	1.26**	31.0	63.0	49.2	[80]
8	$\{NP[OCH_2CF_3]_{0.65}[OCH_2(CF_2)_2CF_3]_{0.35}\}_n$	0.90**	16.0	23.0	68.3	[80]
9	$\{NP[OCH_2(CF_2)_3CF_3]_2\}_n$	1.40**	10.0	64.0	15.5	[80]

*Solvent—tetrahydrofuran.
**Sovent—Freon E-2 (see footnote to Table 3).

According to Hagnauer and Schneider[80], the molecules of the polyfluoroalkoxyphosphazenes investigated are relatively linear and their broad molecular weight distribution must be attributed to the mechanism of the polymerisation of hexachlorocyclotriphosphazene and not to branching. However, this conclusion does not explain the appreciable discrepancies between the molecular weight distributions of specimens Nos.4–6 (Table 4) obtained from polydichlorophosphazene synthesised by the polymerisation of the same amount of the trimer (4 g) under identical conditions.

Carlson et al.[85] also failed to observe an appreciable branching of the macromolecules. They suggest that the broad molecular weight distribution indicates the presence in the polymer of a supermolecular structure of the type of associated species. Thus there is no unanimity among investigators concerning the causes of the broad molecular weight distribution in polyfluoroalkoxyphosphazenes.

In certain cases in the study of the concentration dependence of the intrinsic viscosities of solutions of polyfluoroalkoxyphosphazenes in Freon E-2 an anomalous character of such viscosity was observed, namely an increase of η_{int} with dilution[80]. Furthermore, many specimens had anomalously high Huggins constants (usually more than 1.0) in Freon E-2. The authors attribute these phenomena to the aggregation of the macromolecules owing to the presence in the polymer of groups such as P–OH, >NH, P–O–P, and P=O.

At the same time Aharoni[155] reported recently the discovery of a region of mesomorphous behaviour of solutions of poly[bis(trifluoroethoxy)phosphazene].

Estimates of the glass points of polyfluoroalkoxyphosphazenes yielded extremely interesting results. The data in Table 5 show that low glass points are characteristic of these polymers. This applies also to fluoroalkoxyphosphazene elastomers whose glass points are in the range between −64° and −77 °C.[31]

Table 5. The glass points of polyfluoroalkoxyphosphazenes.

No.	Polymer	T_g, °C	Method*	Refs.
1	$[NP(OCH_2CF_3)_2]_n$	−66	DTA	[36, 37]
	Ditto	−53	TA	[59]
	»	−73	TM	[65]
	»	−70	DTA	[72]
2	$[NP(OCH_2CF_2CF_3)_2]_n$	~−25	DTA	[2, 12, 28]
	Ditto	−76	TM	[65]
3	$\{NP[OCH_2(CF_2)_2CF_3]_2\}_n$	+14	DTA	[2, 12, 28]
	Ditto	−65	TA	[59]
	»	−79	TM	[65]
4	$\{NP[OCH_2(CF_2)_3CF_3]_2\}_n$	−80	TM	[65]
5	$\{NP[OCH_2(CF_2)_5CF_3]_2\}_n$	−63	TM	[65]
6	$\{NP[OCH_2(CF_2)_6CF_3]_2\}_n$	−40	DTA	[72]
7	$[NP(OCH_2CF_2CF_2H)_2]_n$	−75	TM	[65]
8	$\{NP[OCH_2(CF_2)_3CF_2H]_2\}_n$	−64	TA	[59]
	»	−89	TM	[65]
9	$\{NP[OCH_2(CF_2)_5CF_2H]_2\}_n$	−72	TM	[65]
10	$\{NP[OCH_2(CF_2)_2OCF_3]_2\}_n$	−99	TM	[65]
11	$[NP(OCH_2CF_2CHFCF_3)_2]_n$	−67	DTA	[70]

*Methods: DTA = differential thermoanalysis; TA = torsional analysis; TM = thermomechanical tests on A.I.Marei's apparatus[65].

Within the framework of the model of atom–atom potential functions, Allen and Allcock[156] studied the energy surface of polyorganophosphazenes and showed that the potential energy surfaces of polyalkoxyphosphazene molecules, including poly[bis(trifluoroethoxy)phosphazene], contain a large number of minima separated by low barriers. This explains the high flexibility of these polymers and their low glass points T_g. The results of the theoretical calculation are in satisfactory agreement with X-ray diffraction data available for poly[bis(trifluoroethoxy)phosphazene].

At the same time it is striking that the glass points determined by different investigators for the same phosphazene structures show large discrepancies in a number of instances (Table 5, polymer Nos.1, 2, 3, and 8). The causes of these discrepancies are so far obscure but one cannot rule out the possibility that they are associated to a large extent with the non-reproducibility of the results obtained in the synthesis of polyfluoroalkoxyphosphazenes, which has been frequently mentioned in the literature[8,30].

Another interesting feature was observed in the study of the physical transformations in polyorganophosphazenes by scanning calorimetry, the thermoanalytical method, nuclear magnetic resonance, and X-ray diffraction[30,32,59,65,72,157–162], namely the occurrence of two first-order transition temperatures. Table 6 presents the available data concerning this question as regards polyfluoroalkoxyphosphazenes. It is

seen that this aspect of poly[bis(trifluoroethoxy)phosphazene] has been mainly investigated among polyfluoroalkoxyphosphazenes. At the lower transition temperature $T(1)$ the crystalline phase is seen to melt with retention of a definite degree of order, i.e. at $T(1)$ the polymer passes to a mesomorphous state. The upper temperature, at which there is a transition to an isotropic liquid, is the true melting point T_m. In poly[bis(trifluoroethoxy)phosphazene], these two transitions are separated by an unusually wide temperature range amounting to 150 K.[30,32] According to data published recently[65], the width of this range can actually exceed 200 K for certain polyfluoroalkoxyphosphazenes.

Table 6. Thermal transitions in polyfluoroalkoxyphosphazenes.

Polymer	$T(1)$, °C	T_m, °C	Method*	Refs.
$[NP(OCH_2CF_3)_2]_n$	92	240	DSC	[30, 32, 157]
$[NP(OCH_2CF_3)_2]_n$	83	240	DTA	[72]
$[NP(OCH_2CF_3)_2]_n$	68	238	TA	[59]
$[NP(OCH_2CF_3)_2]_n$	83	242	DSC	[65]
$\{NP[OCH_2(CF_2)_2CF_3]_2\}_n$	131	241	DSC	[65]
$[NP(OCH_2CF_2CF_2H)_2]_n$	8	240	DSC	[65]
$\{NP[OCH_2(CF_2)_5CF_2H]_2\}_n$	1	240	DSC	[65]

*DSC = differential scanning calorimetry.

From the practical standpoint, the temperature $T(1)$ is the upper limit of the temperature range in which the polymeric materials can be used. Above $T(1)$, the polymer can be moulded as a thermoplastic, but this entails the displacement of a semirigid structure and not viscous flow.

A more detailed consideration of this phenomenon in polyfluoroalkoxyphosphazenes is not necessary in the present review, since several extremely detailed reviews have been devoted to this question[30,32].

In certain reviews published recently[29,30,32], in the discussion of the question of physical transitions in polyorganophosphazenes under the influence of heat, 360 °C is stated to be the temperature of the onset of the thermal degradation of poly[bis(trifluoroethoxy)phosphazene], determined by thermogravimetric analysis. In reality, the question of the temperature of the onset of the decrease of mass on heating of this polymer is more complex and not quite so unambiguous. This can be illustrated by the data obtained by Connelly and Gilhan[59] and also by Zeldin et al.[75] in a dynamic thermogravimetric analysis of poly[bis(trifluoroethoxy)phosphazene] in an atmosphere of nitrogen. The temperature of the onset of the decrease of mass obtained by the first set of investigators (at a heating rate of 2 K min^{-1}) is ~250 °C, while in the second study (at a heating rate of 5 K min^{-1}) it was close to 350 °C. Such a significant discrepancy between the results cannot naturally be explained solely by the difference between the rates of heating. This is most likely to be associated with definite differences between the chemical structures of the polymer specimens investigated in the two studies.

At the same time, the results of thermogravimetric analysis (TGA) reflect the decrease of mass and yield only preliminary information about the thermal stability of polyfluoroalkoxyphosphazenes. For a deeper investigation of the thermal stability of these polymers, a number of isothermal experiments have been performed with subsequent estimation of the molecular weight characteristics of the test polymers[57,71,82,86]. It was found that, in the temperature range 150–200 °C, polyfluoroalkoxyphosphazenes already undergo a comparatively rapid decrease of viscosity and molecular weight. The dissociation of the polyfluoroalkoxyphosphazene macromolecules in this temperature range takes place at random and is accompanied by a very slight depolymerisation[82].

Such behaviour of polyfluoroalkoxyphosphazenes at comparatively low temperatures is apparently associated with the presence of defective units in their molecules, in particular with the content of unsubstituted P–Cl bonds, branches, etc.

In order to increase the thermal stability of polyfluoroalkoxyphosphazene, zinc and magnesium di(8-hydroxyquinolates)[97,163], zinc and lead dimethyldithiocarbamates[164], and also the zinc derivative of 2-mercaptobenzothiazole[165] have been proposed as stabilisers. Their action involves the deactivation of the defective groups in the polyfluoroalkoxyphosphazene macromolecules by complex formation with units containing the P–Cl, P–OH, and P=O bonds[163].

The data obtained in the study of the photolysis of poly[bis(trifluoroethoxy)phosphazene][72,73] show that this polymer exhibits a high resistance to light. However, the residual unsubstituted P–Cl groups promote the degradation of the polymer, since they increase the amount of light absorbed by the specimen.

Fluoroalkoxyphosphazene polymers are extremely resistant to action of boiling water[55,151]. For example, there are data showing that certain vulcanisates retain ~85% of their initial strength characteristics after 900 h at 100 °C and in 100% relative humidity[151]. In the cold they do not change even after coming into contact with concentrated NaOH and KOH solutions for many months[28,55,151]. The data concerning the action of various acids on polyfluoroalkoxyphosphazenes are extremely contradictory. Thus Rose and Reynard[55] reported that these polymers do not react with concentrated H_2SO_4 at a low temperature. Allcock[28] noted their resistance to glacial acetic acid. However, in a later publication Vicic and Reynard[151] drew attention to the fact that strong inorganic acids and glacial acetic acid impair the mechanical parameters of these polymers. According to these investigators, even dilute acid solutions cause slight hydrolysis of polyfluoroalkoxyphosphazenes. It is noteworthy that all the considerations described above refer to polyfluoroalkoxyphosphazenes tested in the solid state.

Polyfluoroalkoxyphosphazenes do not burn in air. The oxygen index of the flammability of these polymers and materials based on them is 47–65,[83,166] reaching as much as 80 in certain cases[65].

According to Allcock's data[28], poly[bis(trifluoroethoxy)phosphazene] films have effective water repellent properties with a wetting angle of 100 °C and a critical surface tension of 19.7 dyn cm^{-1}. In terms of the latter characteristic, they approach Teflon (22 dyn cm^{-1}) and polydimethylsiloxane (18 dyn cm^{-1}).[28] Allcock[28] notes that poly[bistrifluoroethoxy)phosphazene] and poly[bis(pentafluoropropoxy)phosphazene] films are very flexible and can be readily oriented on extension, giving rise to material with a high tensile strength. At the same time, Singler et al.[8] characterised poly[bis(trifluoroethoxy)phosphazene] as an elastic but weak material. Materials having a tensile strength of 175 kg cm^{-1} with 200% elongation on rupture have been obtained on the basis of fluoroalkoxyphosphazene elastomers, but, overall, a tensile strength of ~100 kg cm^{-2} accompanied by 100–200% elongation is more characteristic of such vulcanisates[31].

As regards the possible applications of polyfloroalkoxyphosphazenes, one should note in the first place their likely usefulness as oil- and petrol-resistant elastomeric materials with an improved fire resistance over a wide range of working temperatures combined with an effective frost resistance. In particular, compositions based on vulcanised elastomers are being developed at the present time for sealing devices in oil seals, sleeves, washers, fuel hose, etc. in the working temperature range from −60 to +200 °C.[8, 31,83,151]. The application of polyfluoroalkoxyphosphazenes in the textile industry has been proposed. It involves the impregnation of textiles with these polymers in order to impart to them water- and dirt-repellent properties[167]. At the same time, there exist patent data according to which polyfluoroalkoxyphosphazenes can be used as binders in compositions for water-impermeable galvanic cells[168–171] and for electrodes in chemical cells[172].

Studies of the possible applications of poly[bis(trifluoroethoxy)phosphazene] in the solution of the problem of resistance to thrombosis and biocompatibility are of undoubted interest[33,34,172,173]. Preliminary selective tests *in vitro*[33] and also *in vivo*[34] enabled the authors to conclude that further studies of polyfluoroalkoxyphosphazenes from the standpoint of their possible use in medicine are desirable. At the same time it has been shown that the high resistance to thrombogenesis in contact with native blood and the contancy of the physicochemical and mechanical properties after prolonged contact with a medium close in composition to blood make these polymers extremely promising for vascular surgery[173].

Such a wide variety of properties, which are promising from the practical point of view, makes it possible to classify polyfluoroalkoxyphosphazenes as polymers with a wide range of purposes, which is apparently the reason for the increased interest in these polymers during the last 15 years.

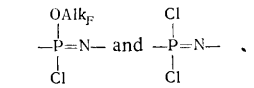
Overall, analysis of the literature data on the properties of polyfluoroalkoxyphosphazenes permits the following conclusions. On the one hand, polyfluoroalkoxyphosphazenes are undoubtedly interesting polymers with a wide variety of valuable properties. On the other hand, in the analysis of these properties attention is drawn in many instances to their very significant non-reproducibility. Therefore, some of the results achieved at the present time undoubtedly cannot as yet be regarded as optimal. The non-reproducibility of many properties of these polymers can be caused in the first place by the formation of anomalous units during synthesis which can influence their properties. This resembles the situation demonstrated by Korshak[174], for many heterounit organic polymers. Bearing this in mind, we thought it useful to consider this problem specially.

IV. THE INFLUENCE OF THE HETEROUNIT STRUCTURE OF POLYFLUOROALKOXYPHOSPHAZENES ON THEIR PROPERTIES

The heterounit structure of polyfluoroalkoxyphosphazenes can arise during their synthesis for several reasons and its chemical nature can be diverse. In the first place it is due to the branching inherited from the initial polydichlorophosphazene. This type of heterounit structure can, however, be virtually eliminated by employing as the starting material the linear polydichlorophosphazene obtained in accordance with the method developed recently for the polymerisation of hexachlorocyclotriphosphazene in a preheated polymerisation system[50,51].

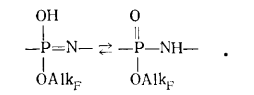
Another type of heterounit structure arises owing to the incomplete substitution of chlorine in the initial dichlorophosphazene, which, like, incidently, the majority of other macromolecular reactions[175], does not go to 100% completion. On this basis, one can assume that polyfluoroalkoxyphosphazene contain, together with units of the dominant type

also various amounts of intermediate and initial units:

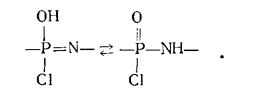


Since very high degrees of substitution (>99%) are nevertheless as a rule comparatively readily attained in the synthesis of polyfluoroalkoxyphosphazenes, it is natural to expect that their molecules contain mainly anomalous intermediate units with one unsubstituted chlorine atom at the phosphorus atom. However, in a study of the photolysis of poly[bis(trifluoroethoxy)phosphazene], Ferrar et al.[73] detected *gem*-1,1-$N_3P_3Cl_2(OCH_2CF_3)_4$ in the degradation products together with a cyclic trimer fully substituted by trifluoroethoxy-groups. This constitutes direct evidence for the presence in the polymer also of anomalous initial units with two unsubstituted chlorine atoms at the phosphorus atom. The amount of residual chlorine in polyfluoroalkoxyphosphazenes is a measure of the overall content of anomalous units with unsubstituted P–Cl groups.

We have shown[66–68] that yet another very significant type of heterounit structure can arise owing to the occurrence of hydrolytic side reactions in the synthesis of polyfluoroalkoxyphosphazenes. The anomalous units formed in this process can be present in the polymer in two tautomeric forms:



In addition, there is also a possibility of the combination of heterounit structures of different chemical types involving a single anomalous unit:

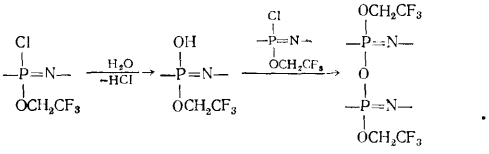


Such wide variety of anomalous units makes it significantly difficult to obtain stable readily reproducible results in the synthesis of polyfluoroalkoxyphosphazenes. This has led to the necessity for the investigation of the influence of the number and nature of the anomalous units on the set of properties of polyfluoroalkoxyphosphazenes. The study of hydrodynamic, conductimetric, and dielectric properties of dilute solutions of poly[bis(trifluoroethoxy)phosphazene] with different heterounit structures[176–178] by three independent methods led to the discovery of previously unknown polyelectrolyte properties of polyfluoroalkoxyphosphazenes in solution in organic solvents and showed that the presence of the specific amount of anomalous units with P–Cl and P–OH groups leads to the appearance of ionogenic groups in these polymers. An important feature of the polymers is the high sensitivity of their properties to small amounts of anomalous units (<1 mole %).

An electron microscope study of dilute solutions of poly[bis(trifluoroethoxy)phosphazene][179] made it possible to obtain more complete information about the character of the acquisition of polyelectrolyte properties by a polyfluoroalkoxyphosphazene, showing that, in dilute solutions in

polar and moderately polar solvents of the type of acetone and THF, poly[bis(trifluoroethoxy)phosphazene] exists in the form of individual macromolecules and that the formation of ionised groups in it is predominantly intramolecular.

The presence of anomalous units with residual P–Cl groups as well as very small amounts of P–OH and P(O)–NH groups, arising as a result of hydrolytic side reactions, reduces significantly the hydrolytic stability of poly[bis(trifluoroethoxy)phosphazene][66,67]. For example, the polymer containing ≥0.2 wt.% of unsubstituted chlorine is hydrolytically so unstable that it loses its solubility in organic solvents even at room temperature. The loss of solubility is associated in this instance with the formation of cross-links between the macromolecules of poly[bis(trifluoroethoxy)-phosphazene] in accordance with the following scheme:



When the chlorine content is <0.2 wt.%, the polymer is hydrolytically more stable. However, when the chlorine content is in the range 0.06–0.20 wt.%, an appreciable decrease of [η] is nevertheless observed after boiling the polymer in aqueous acetone (at 56 °C), i.e. at a comparatively low temperature. Only in those cases where the amount of unsubstituted chlorine in poly[bis(trifluoroethoxy)phosphazene] does not exceed 0.06 wt.%, which corresponds (without taking into account other anomalous units) to a chlorine content of 0.21 mole %, is the polymer hydrolytically stable also on boiling in aqueous acetone.

All the factors described above are valid only when the polymer contains virtually no partly hydrolysed fragments. Their presence has the same unfavourable influence on the hydrolytic stability of polyfluoroalkoxyphosphazenes as the presence of unsubstituted P–Cl groups. Consequently, the hydrolytic stability of polyfluoroalkoxyphosphazenes at moderately high temperatures depends on the overall content of all the anomalous units with P–Cl, P–OH, and P(O)–OH groups. This conclusion has a direct bearing on the stability and reproducibility of the results, which had not been taken into account previously in the synthesis of polyfluoroalkoxyphosphazenes. To ensure the stability and high reproducibility of the results in the synthesis of such polymers, the overall content of the anomalous units should not exceed 0.2 mole %. Therefore, the valuable properties of polyfluoroalkoxyphosphazenes, characteristic of units of the dominant type, can be achieved only when a very far-reaching polymer-analogue substitution reaction is carried out under conditions ensuring a virtually total absence of hydrolytic side reactions and a minimal hetero-unit structure of these polymers.

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Nesmeyanov Institute of
Organoelemental Compounds,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 107-134 (1984) U.D.C. 678.86 : 546.27

Latest Advances in the Field of Carbaborane-containing Polymers

N.I.Bekasova

The results of studies of carbaborane-containing polymers with different structures, carried out in the last six years, are surveyed. The methods of synthesis of carbaborane-containing polymers, their physicochemical properties, and their practical applications are considered.
The bibliography includes 128 references.

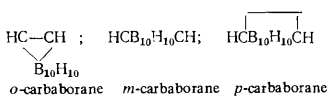
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I. INTRODUCTION

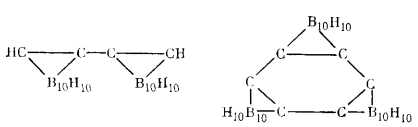
Carbaborane-containing polymers have already been known for approximately twenty years. Many of these unusual and very interesting polymers are capable of withstanding extremely severe conditions under which the organic polymers decompose almost completely.

The latest review on the synthesis and properties of carbaborane-containing polymers, included in the book "Advances in the Synthesis of Organoelemental Polymers"[1], contains data published between 1966 and 1976 inclusive. The chemistry of carbaborane-containing polymers is nowadays continuing to develop vigorously. The aim of the present review is to survey data which have been published from 1977 to 1982; the review also includes articles published in 1977 but not included in the earlier review[1]. In order to make it easier to become acquainted with the new advances in the study of carbaborane-containing polymers of different structure, the data surveyed are arranged in the same sequence as in Korshak's book[1]. Three isomeric forms of carbaborane have come to be represented in the following manner[1]:



II. POLYCARBABORANYLENES

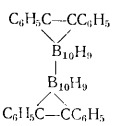
There are no examples in the literature of the specific synthesis of polycarbaboranylenes (i.e. polymers in which the carbaborane fragments are connected directly to one another via a C—C, B—C, or B—B bond). However, the condensation of carbaboranes with evolution of H_2 and the formation of oligomers has been described in some studies. Thus, when *o*-carbaborane was exposed to γ-radiation at 31 °C, the formation of dimers and trimers with a C—C bond and having the following structure was observed[2]:



A cyclic *o*-carbaborane trimer has also been detected in the γ-radiolysis of 1-phenyl-*o*-carbaborane (at 31 °C), which is accompanied by the evolution of benzene[3]. Under analogous conditions, partial isomerisation of *o*-carbaborane to *m*-carbaborane and of *m*-carborane to *o*-carbaborane, accompanied by the formation of dimeric and polymeric products (yield ~ 24%), was observed[4]. The authors believe that the polymers have a complex composition: both the polymers obtained on exposure of *o*-carbaborane to γ-radiation and the polymers derived from *m*-carbaborane contain isomeric *o*- and *m*-carbaborane fragments.

The formation of polycarbaboranylenes with an assumed B—B bond was also noted on heating *o*-, *m*-, or *p*-carbaborane *in vacuo* at temperatures above 600 °C.[5]

It is known that, when carbaboranes are heated in air at ~250 °C, they are oxidised with formation of B—OH and B—O—B bonds[6]. The formation of a dimer with a B—B bond, observed[7] on heating diphenyl-*o*-carbaborane in air in the temperature range 260–330 °C, is therefore extremely unusual. The structure of the dimer



was confirmed by gas–liquid chromatographic, mass-spectrometric, and ebullioscopic data.

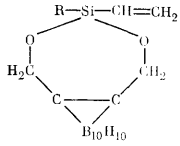
III. CARBOCHAIN POLYMERS

The synthesis and study of carbochain polymers and copolymers containing carbaborane groups in the side chain continues to attract the attention of investigators. Few studies devoted to the homopolymerisation of alkenylcarbaboranes have been published. Steric hindrance due to the bulky carbaborane groups is manifested[1] in the homopolymerisation of 1-alkenyl-*o*-carbaboranes. In addition, the electron density in the double bond diminishes due to the highly electron-accepting *o*-carbaborane fragments. For this reason, 1-alkenyl-*o*-carbaboranes polymerise less effectively the closer is the double bond to the carbaborane group. The hypothesis that the free-radical oligomerisation of 1-alkenyl-*o*-carbaboranes can lead to the formation of two different oligomers has been confirmed with the aid of a

quantum-chemical calculation of the charge distribution in 1-alkenyl-*o*-carbaboranes[8]. One of the oligomers consists of a polyethylene chain with the *o*-carbaboranyl group in the side chain, while the second oligomer contains the *o*-carbaborane fragment in the main chain.

The capacity of 4-(1-*o*-carbaboranyl)styrene for homopolymerisation under various conditions has been investigated[9]. Polymers with the highest molecular weight [$M \cong 60\,000$, softening temperature (soft.temp.) 280–340 °C] have been synthesised by the thermopolymerisation of 4-(1-*o*-carbaboranyl)styrene at 160–200 °C. In the presence of radical initiators (for example, t-butyl peroxide) polymers with $M \cong 12\,000$ and a softening temperature of 320–340 °C are formed. The homopolymerisation of 4-(1-*o*-carbaboranyl)-styrene via an anionic mechanism in the presence of C_4H_9Li takes place slowly, while the polymerisation via a cationic mechanism in the presence of $BF_3.O(C_2H_5)_2$ does not occur at all. From the infrared spectra of the polymers obtained, one can assume that the homopolymerisation of 4-(1-*o*-carbaboranyl)styrene proceeds in all cases mainly via the vinyl group. Thermogravimetric analysis of these polymers has shown that the weight loss by their specimens is ~20% at 400–430 °C.

The study of the homopolymerisation of *o*-carbaborane-containing exocyclic vinylsilanes with various substituents R at the silicon atom has been described[10]:



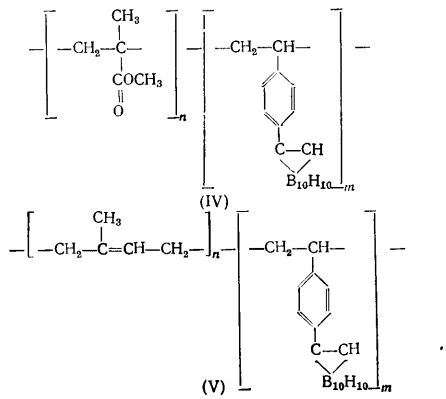
R = CH_3 (I); OCH_3 (II); Cl (III).

It has been established that the homopolymerisation of compound (I) in bulk (a mixture of benzoyl and t-butyl peroxides was used as the initiator) proceeds via the vinyl group with formation of a dimer. The homopolymerisation of compounds (II) and (III) via the vinyl group is accompanied by the partial substitution of the $SiOCH_3$ and SiCl groups by SiOH and the partial dissociation of one of the SiO bonds; this results in the formation of a mixture of dimers, trimers, and cross-linked oligomers. The latter are obtained on interaction of the SiOH groups with $SiOCH_3$ and SiCl. The formation of oligomers alone, and not polymers, has been explained[10] by the steric hindrance generated by the seven-membered exocyclic groups. All the homopolymers are colourless viscous liquids.

The copolymerisation of compounds (I), (II), and (III) with methyl acrylate takes place more readily. It has been carried out under the same conditions as the homopolymerisation[10]. The content of the initial vinylsilanes in the reaction mixture varies from 1 to 20 mole %. Solid glass-like substances with *M* ranging from 400 000 to 800 000 were obtained in all cases. Compound (II) proved to be the most reactive of the monomers; after the introduction of compounds (I), (II), and (III) into the reaction mixture in an amount of 20 mole %, the contents of their unit in the copolymers were 9, 12, and 3 mole % respectively.

The copolymerisation of 1-vinyl-*o*-carbaborane with styrene (in proportions of 1 : 3) under the influence of γ-rays has been investigated[11]. It was established that the copolymer consists of 11 or 12 units and that there are approximately 9 styrene units for each two 1-vinyl-*o*-carbaborane units. The copolymer softens at 85 °C and melts fully at 105 °C. Its structure was investigated with the aid of NMR and flash pyrolysis methods. However, the authors[11] were unable to determine the location of the *o*-carbaborane fragment (in the main or side chain).

New copolymers having the following structure have been synthesised on the basis of 4-(1-*o*-carbaboranyl)styrene and methyl acrylate[12]:



(IV)

(V)

The copolymers were obtained in 80–90% yield in bulk on heating the monomers to 80 °C in the presence of radical type initiators (t-butyl peroxide and azobisisobutyronitrile). The molecular weight of the copolymers (IV) increases from 3460 to 7130 as the ratio of 4-(1-*o*-carbaboranyl)styrene and methyl methacrylate is altered from 1 : 1 to 1 : 4, while the molecular weight of the copolymers (V) increases from 3550 to 278 000 as the ratio of 4-(1-*o*-carbaboranyl)styrene and isoprene is altered from 1 : 1 to 1 : 10. The influence of the heterounit structure (i.e. the ratio of the numbers of units *n* and *m*) on the glass point and on the onset of intense loss of weight has been analysed[12]. It has been shown that the thermal characteristics of the copolymers (IV) vary additively with the extent of their heterounit structure, while for the copolymers (V) the relation is non-additive.

Copolymers containing hydroxy- or carboxy-groups have been synthesiseed by the copolymerisation of 1-vinyl-*o*-carbaborane, 1-isopropenyl-*o*-carbaborane, or 1-acryloyloxymethyl-*o*-carbaborane with isoprene, butadiene, or chloroprene in solution in dioxane at 65 °C for 72 h in the presence of 4,4'-azobis(4-cyano-1-pentanol).[13] The authors note that the large difference between the polarities of the selected co-monomers ensures ease of copolymerisation. In all cases an increase of the content of unsaturated *o*-carbaborane derivatives in the reaction mixture from 5 to 50 wt.% entails a decrease of the yield and molecular weight of the copolymers. For example, the yield of the copolymer of acryloyloxymethyl-*o*-carbaborane with chloroprene decreases from 85 to 70% and its molecular weight decreases from 7400 to 4300.

The copolymers, which can be used as plasticisers and catalysts of the combustion of solid rocket fuels, have been obtained by the aqueous emulsion copolymerisation of methacryloyloxymethyl-*o*-carbaborane with butadiene in the presence of azobisisobutyronitrile, dodecanethiol, and benzylacetyldimethylammonium chloride at 50 °C with vigorous stirring[14]. Depending on the ratio of the comonomers, the copolymers contain 10–80 mole % of butadiene units and 90–20 mole % of methacryloyloxymethyl-*o*-carbaborane.

In order to modify low-density polyethylene, a study has been made of the radical copolymerisation of ethylene with 1-isopropenyl-*o*-carbaborane in an autoclave at a pressure of 1400 kg cm^{-2} and a temperature of 160 °C.[15] It has been established by infrared spectroscopy that the copolymerisation involves mainly the double bonds and that its rate and the molecular weight of the copolymers decrease rapidly with increase of the content of the *o*-carbaborane derivatives in the reaction mixture from 1 to 40 mole %. All the copolymers

obtained in this way are solid plastics soluble in aromatic hydrocarbons and capable of being pressed at 130–170 °C to form transparent elastic films. The specimens containing 2–3 mole % of 1-isopropenyl-*o*-carbaborane had a tensile strength and a relative elongation on extension of not less then 100 kg cm^{-2} and 300% respectively. With increase of the content of 1-isopropenyl-*o*-carbaborane in the copolymer, the density of the latter also increases (to 1 g cm^{-3}) and its thermo-oxidative stability improves. The effect of γ-radiation on copolymers containing 0.28–0.30 mole % of 1-isopropenyl-*o*-carbaborane has been investigated[16]. Measurements of the properties related to the strength of the copolymers have shown that their radiation stability is close to that of polyethylene. The resistance of the copolymers to oxidation diminishes after γ-irradiation.

The interaction of a chloromethylated polystyrene–divinylbenzene copolymer with lithio-*o*-carbaborane has been described[17]; on the basis of the results of elemental analysis for boron, the authors assume that the chlorine atoms in at least three-quarters of the chloromethyl groups have been substituted by the *o*-carbaboranyl groups.

Data on the use of polymers and copolymers based on various alkenylcarbaboranes in adhesives for the improvement of their thermal stability[18,19] and for the preparation of anion-exchange resins[20] are presented in the patent literature.

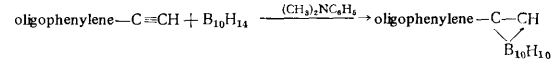
The copolymers of the diallyl esters of *m*- or *p*-carbaboranedicarboxylic acids and methyl methacrylate have been recommended as materials suitable for use in an atmosphere of oxygen at elevated temperatures[21].

IV. POLYMERS OF THE POLYPHENYLENE TYPE

A large number of publications devoted to the synthesis and investigation of polymers of the polyphenylene type, containing carbaborane fragments in both side and main chains, have appeared in recent years. Thus, after radiolysis, 1-phenyl-*o*-carbaborane was found to undergo oligomerisation as a result of the abstraction of hydrogen from the benzene ring with formation of dimers, trimers, and tetramers[3].

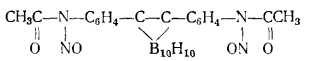
The polycondensation of 1,2-diphenyl-*o*-carbaborane in the presence of Lewis acids and oxidising agents yielded an oligomer with $M = 1300$, soluble in benzene and chloroform and not melting up to 350 °C.[22] According to thermogravimetric data, the mass of the specimen of the oligophenylene obtained does not change up to 500 °C; at 900 °C the weight loss is 11.6%.

Oligophenyl-*o*-carbaboranes, which are amorphous pale-brown powders readily soluble in the usual organic solvents, have been synthesised by the reaction of oligophenylene containing terminal triple bonds with decaborane in accordance with the following scheme[23]:

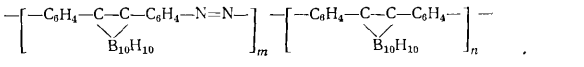


Infrared spectroscopic data and the results of elemental analysis have shown that the replacement of the ethynyl linkages in the oligophenylene by *o*-carbaborane fragments takes place almost quantitatively. The absence of residual ethynyl groups from the oligophenyl-*o*-carbaborane is responsible for its complete inability (in contrast to the usual oligophenylene) to pass to an infusible and insoluble state on heating to 300 °C. The oligophenylene-*o*-carbaboranes are characterised by a higher thermal stability (both in an inert atmosphere and in air) than the initial oligophenylenes. The yield of the carbon residue is 84.5% for oligophenylene-*o*-carbaborane at 900 °C according to thermogravimetric data, while the yield for the usual oligophenylene under analogous conditions is 68%.

The recombination of the phenyl and azophenylene decomposition products of 1,2-bis(*N*-nitrosoacetamidophenyl)-*o*-carbaborane



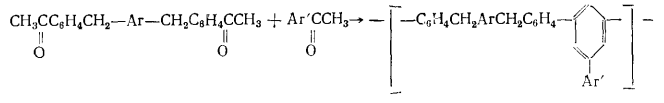
resulted in a quantitative yield of a *o*-carbaborane-containing polyazophenylene having the following structure[24–26]:



This polymer is a pale-brown powder soluble in chloroform, benzene, dimethylformamide, and tetrahydrofuran. Its structure has been confirmed by elemental analysis and infrared and ultraviolet spectroscopy. On isothermal heating at 400 °C in an atmosphere of helium, the mass of the polymer specimen initially decreases rapidly by ~10% and then remains almost unchanged for 3 h. According to the results of dynamic thermogravimetric analysis in air, polyazophenylene with *o*-carbaborane fragments is stable up to 350 °C and above this temperature there is an appreciable increase in the mass of the polymer specimens (up to 30% at 600 °C) owing to the oxidation of B–H groups and the formation of the B–O–B groups.

The ability of the *o*-carbaborane fragments of polyazophenylene to combine vigorously with O_2 at high temperatures with formation of inactive products can be used, according to the authors[25,26], for the inhibition of the thermo-oxidative degradation of thermostable polymers. Indeed, the copolymers of styrene with the decomposition products of 1,2-bis(*N*-nitrosoacetamidophenyl)-*o*-carbaborane, containing between 4 and 38 wt.% of polyazophenylene fragments, exhibit a high thermo-oxidative stability at 400–450 °C.[24]

Polyphenylenes, the first stage of the synthesis of which can be represented schematically by the reaction



(where Ar = *o*-, *m*-, or *p*-carbaboranylene and Ar′ = phenyl or benzyl-*o*-, -*m*-, and -*p*-carbaboranyl) have been obtained by Korshak and co-workers[27–29] by the joint polycyclocondensation of 4,4′-diacetyldibenzyl-*o*-, -*m*-, and -*p*-carbaboranes and various aromatic monoacetyl derivatives (in benzene at 20 °C in the presence of gaseous HCl as the catalyst) with subsequent heat treatment. Instead of acetyl derivatives, their ethylketals can be used in the reaction.

Korshak and co-workers[27–29] noted that the polycyclocondensation of the above compounds does not proceed unambiguously and is accompanied by the formation of dypnone as well as linear and cyclic polyvinylene fragments. The oligophenylenes obtained in this way, containing *o*-, *m*-, or *p*-carbaborane groups in the main molecular chain and in certain cases also in the side chain, are readily soluble in many organic solvents and in chloroform the oligomer concentration can be more than 20%.

All the carbaborane-containing oligophenylenes have low molecular weights ($\bar{M}_n = 1100–4600$), but their fractionation yielded a fraction with $\bar{M}_w = 115\,000$.[27,28] According to the results of thermomechanical studies, the softening temperature of the oligophenylenes synthesised is in the range 150 to

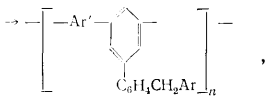
220 °C; at 400–500 °C in an inert atmosphere in the course of 4 h or during pressing with heating up to 400–450 °C at a pressure of 1000 kg cm^{-2}, they are converted into infusible and insoluble three-dimensional polymers as a result of the interaction via the terminal acetyl and ketal groups. According to infrared spectroscopic data, there are no ketal, acetyl, or dypnone groups in the hardened polymers.

The results of thermogravimetric analysis showed that the mass of the heat-treated polymer specimens increases by up to 18% at 400 °C in air as a consequence of the oxidation of the carbaborane groups at the B–H bond. On further increase of temperature to 1000 °C, an appreciable change in the mass of the specimen is not observed. The high thermal stability of the polymers, which are not deformed up to 450 °C, has been noted[27,28]. Detailed study of the properties of the oligophenylenes obtained from derivatives of isomeric carbaboranes enabled the authors[27,28] to conclude that the solubility and thermal stability of the oligomers synthesised are almost independent of the carbaborane isomer from which they have been obtained.

Polyphenylenes with *o*-, *m*-, or *p*-carbaborane fragments in the main chain exhibit an improved adhesion to glass fibre, amounting to 250–350 kg cm^{-2}, and have been recommended for use as thermostable binders for glass plastics[29].

Korshak and co-workers[27,30] also obtained oligophenylenes containing carbaborane fragments in the side chain by the polycondensation of the ethylketals of 4-acetylbenzyl-*o*-, -*m*-, or -*p*-carbaboranes with various ethylketals of aromatic diacetyl derivatives in accordance with the scheme

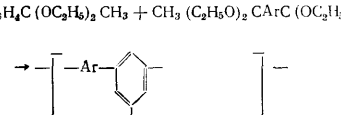
$$ArCH_2C_6H_4C(OC_2H_5)_2CH_3 + CH_3C(OC_2H_5)_2Ar'C(OC_2H_5)_2CH_3 \rightarrow$$



where Ar = *o*-, *m*-, or *p*-carbaboranyl and Ar′ = C_6H_4, $C_6H_4C_6H_4$, or $C_6H_4CH_2C_6H_4$. All the oligophenylenes synthesised in this way have low molecular weights (M = 1400–3200) and are readily soluble in organic solvents such as benzene, toluene, or dioxane and harden at 400–450 °C with formation of three-dimensional polymers. According to thermogravimetric data obtained in air, the mass of the specimens of the hardened polymers begins to decrease in the temperature range 550–600 °C.

The authors[27,30] noted that the introduction of carbaborane fragments into the polyphenylene side chain increases their thermal stability but this effect is smaller than in polyphenylenes containing carbaborane groups in the main macromolecular chain. In order to simplify the synthesis of polyphenylenes with *o*-carbaborane fragments, 4-acetylbenzoyl-*o*-carbaborane, whose synthesis is also technologically complex, has been replaced recently by the more readily available ethylketal of acetylbiphenylyl-*o*-carbaborane:[31,32]

$$HC(B_{10}H_{10})C{-}C_6H_4C_6H_4C(OC_2H_5)_2CH_3 + CH_3(C_2H_5O)_2CArC(OC_2H_5)_2CH_3 \rightarrow$$



;

Ar = C_6H_4, $C_6H_4C_6H_4$, $C_6H_4OC_6H_4$, $C_6H_4SC_6H_4$, $C_6H_4CH_2C_6H_4$.

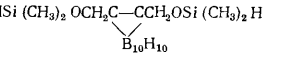
It has also been suggested that the replacement of the methylene bridge by a phenylene bridge on passing from 4-acetylbenzyl-*o*-carbaborane to acetylbiphenylyl-*o*-carbaborane increases the thermal stability of the final polymers.

The polycondensation of acetylbiphenylyl-*o*-carbaborane with the ethylketals of various aromatic acetyl derivatives has been carried out at temperatures between −20° and 150 °C in benzene or dichlorobenzene, toluene-*p*-sulphonic acid being used as the catalyst instead of gaseous HCl at 100 °C and above[31,32]. Infrared spectroscopic data for the oligophenylenes obtained showed that the macromolecules contain the dypnone fragments

and in an amount greater than in oligophenylenes without *o*-carbaborane fragments.

The oligophenylenes synthesised from acetylbiphenylyl-*o*-carbaborane were less soluble than oligphenylenes based on 4-acetylbenzyl-*o*-carbaborane: they dissolved fully only in chloroform and *o*-dichlorobenzene and were insoluble in benzene, toluene, and dioxane. However, their thermal stability did indeed prove to be higher than those of oligophenylenes based on 4-acetylbenzyl-*o*-carbaborane.

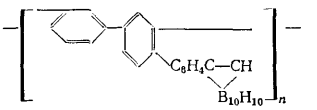
In order to optimise the structure formation process in polyphenylenes with terminal acetyl groups, a study has been made[33] of their interaction with the following di(hydroxymethyl)-*o*-carbaborane derivative:



It was established that at 200–300 °C the acetyl groups of polyphenylene interact with the above compound to form cross-linked monomers whose thermal stability is analogous to that of polyphenylene heat-treated at 450 °C without additives.

The use of *o*-carbaborane-containing polyphenylenes as binders for thermostable glass plastics[33] and for the manufacture of constructional materials[34] has been described.

In addition, *o*-carbaborane-containing oligophenylenes having the structure

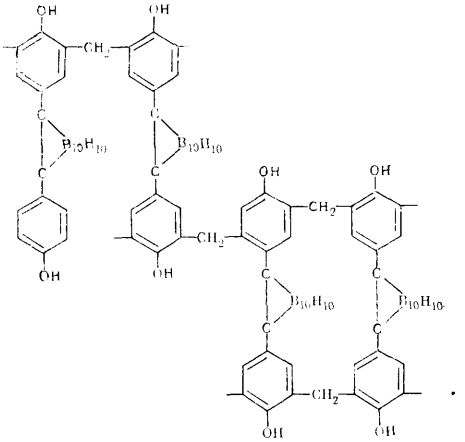


have been considered[35] as the ligands for the synthesis of π-arenechromium carbonyl complexes.

V. PHENOL-FORMALDEHYDE POLYMERS

Studies on the synthesis and properties of carbaborane-containing phenolformaldehyde polymers have continued in recent years. Mixed phenol-formaldehyde polymers of the resol type, based on 1,2-di(4-hydroxyphenyl)-*o*-carbaborane and phenol, whose molar ratio was varied from 1 : 3 to 1 : 21, have been synthesised and thoroughly investigated[36–39]. In contrast to resol, which is based solely on 1,2-di(4-hydroxyphenol)-*o*-carbaborane and hardens at 200–220 °C, mixed *o*-carbaborane-containing resols exhibit an enhanced fluidity (the softening temperatures are in the range 60–110 °C) and harden under the conditions usual for phenol-formaldehyde resols. With decrease of the content of the *o*-carbaborane fragments in the resol, its softening temperature diminishes from 110° to 60 °C, the mass of the coke residue falls from 61% to 18% on heating in air to 900 °C, and the molecular weight increases from 650 to 800.

From data obtained by NMR and infrared spectroscopy, the following structure has been proposed[39] for the resol based on 1,2-di(4-hydroxyphenol)-*o*-carborane hardened at 250 °C for 1 h:



The chemical reactions occurring in resols and resites based on 1,2-di(4-hydroxyphenyl)-*o*-carbaborane on heating in the range 50–450 °C in air and *in vacuo* have been investigated[37]. It was established that at 50–200 °C structure formation in the *o*-carbaborane-containing resol proceeds via the mechanism usual for resols and the *o*-carbaborane groups do not undergo significant transformations, the degree of reaction depending on the heating conditions (in air or *in vacuo*).

From the results of elemental analysis and infrared spectroscopic data as well as studies of the thermo-oxidative degradation of a number of model compounds, it has been suggested[37] that the large carbon residue from the *o*-carbaborane-containing resites is caused either by the oxidation of the B–H group in the *o*-carbaborane nuclei or by the interaction of the *o*-carbaborane fragments with atmospheric moisture and the phenolic hydroxyls and the inhibition of the thermo-oxidation of the organic fragments of the resites in the presence of *o*-carbaborane groups or the products of their thermal or thermo-oxidative reactions.

In order to elucidate the nature of the high thermal stability of the *o*-carbaborane-containing resites, their EPR spectra were investigated[38,40] and a study was made of their structural transformations by X-ray diffraction after heat treatment in the temperature range 200–1200 °C.[41] The results confirmed that both the oxidation of the B–H group of the *o*-carbaborane fragment and other processes associated with the consumption of these groups are most characteristic of *o*-carbaborane-containing resites at temperatures above 400 °C. An appreciable amount of hydrogen is evolved and the three-dimensional polymer network is compacted as a result of the formation of strong B–B, B–O–B and possibly B–C linkages. By virtue of the presence of the thermally stable macronetwork system, the resulting radicals are therefore unable to emerge from the "cage" and undergo secondary recombination processes. It has been suggested[40] that the hydrogen split off from the B–H bond can interact with the radicals, inhibiting further polymer decomposition processes.

Adhesives whose main strength characteristics are not reduced after prolonged (500 h) ageing at 500 °C have been prepared on the basis of *o*-carbaborane-containing resol resins[42]. There are tentative data concerning the synthesis of phenol-formaldehyde resins based on phenolphthalein *N*-[4-(*o*-carbaboranyl)phenyl]imide, which have been recommended as thermostable binders[43], and concerning the use of di[*N*,*N*'-di(hydroxymethyl)aminophenyl]-*o*-carbaborane for the hardening of phenol-formaldehyde oligomers[44].

VI. HETEROCHAIN POLYMERS

1. Polyesters

The number of studies on the synthesis of carbaborane-containing polyesters has diminished while the number of publications devoted to the investigation of the properties of the previously synthesised polyesters with carbaborane fragments remains comparatively large.

Korshak and co-workers described the synthesis of unsaturated carbaborane-containing polyesters[45]. Polyesters having different structures were synthesised, their boron content varying from 1 to 33 wt.%, which corresponds to the variation of the ratio of the number of carbaborane fragments to the number of unsaturation centres from 1 : 36 to 1 : 1. The starting compounds were *m*- and *p*-carbaboranedicarboxylic acids or their dichlorides, maleic anhydride, and various saturated and unsaturated aliphatic glycols such as ethylene glycol, hexamethylene glycol, but-2-enediol, but-2-ynediol, triethylene glycol, and tetraethylene glycol. All the carbaborane-containing unsaturated substances obtained proved to be oligomers having molecular weights ranging from 1400 to 6300 and readily soluble in organic solvents. Most of them readily copolymerise with styrene and form cross-linked polymers whose decomposition temperatures were in the range 275–400 °C. It has been established[45] that the thermal stability of the polymers synthesised depends mainly on the structure of the initial glycol and that the variation of the amount of boron in the polymer from 1 to 19 wt.% does not have a significant influence.

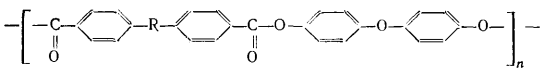
Thermostable adhesive compositions with a shear strength of 330 kg cm^{-2} at 25 °C and 50–60 kg cm^{-2} at 250 °C have been obtained from unsaturated polyester-*m*-carbaboranes containing 2–3 wt.% of boron[45]. In addition, the same polyesters containing 5–11 wt.% of boron were used to obtain an optical adhesive thermally stable up to 250 °C and ensuring the formation of a transparent adhesive seam with a transmittance coefficient up to 92% in the wavelength range 0.4–1 μm.[46]

The reaction of 1,2- or 1,7-di(hydroxymethyl)carbaborane with 1,3-di(10-carboxydecanyltetramethyldisiloxane yielded *o*- and *m*-carbaboranesiloxane polyesters[47]:

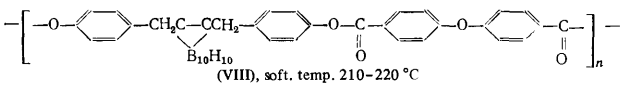
$$\mathrm{HOCH_2RCH_2OH} + \mathrm{HOC(CH_2)_{10}Si(CH_3)_2OSi(CH_3)_2(CH_2)_{10}COOH} \rightarrow \text{polyester.}$$

where R = *o*-carbaboranylene or *m*-carbaboranylene. The study of the kinetics of this polycondensation reaction showed that the introduction of the carbaborane fragments into the macromolecular chain greatly reduces the rate of formation of the polymers and the rate of reaction of the dibasic acid with 1,7-di(hydroxymethyl)-*m*-carbaborane is higher than that of the reaction with 1,2-di(hydroxymethyl)-*o*-carbaborane. It has been suggested[47] that the thermal stability of the carbaboranesiloxane polyesters is not inferior to that of the carbaborane-containing polyarylates, but, in contrast to the latter, they have lower softening temperatures. They are soluble in many solvents.

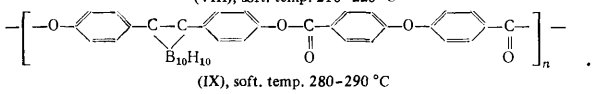
A number of studies[48–56] have been devoted to the carbaborane-containing polyesters with the following structure described previously:



R = *o*-carbaboranylene [compound (VI), soft. temp. 260–280 °C] or *m*-carbaboranylene [compound (VII), soft. temp. 240–260 °C]



(VIII), soft. temp. 210–220 °C



(IX), soft. temp. 280–290 °C

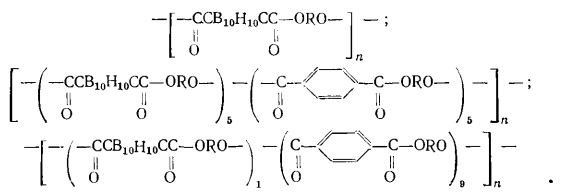
The kinetics of sorption and structural transformations in the tetrahydrofuran-polymers (VI)–(IX) systems have been investigated and it has been shown that the sorption of tetrahydrofuran vapour entails an improvement of the amorphous structure of the polymer, while in the case of polymers tending to crystallise there is a transition from the amorphous to a partly crystalline state[49]. The authors note that during the sorption of tetrahydrofuran vapour only the polymer (IX) crystallises. The latter phenomenon agrees well with the result of a study (by the dipole moment method) of the structures of low-molecular-weight compounds which serve as models of the polymers investigated[50]. It was established that the polymer (IX) can be represented by only one conformer, while a set of conformers is characteristic of other polymers.

In addition it has been shown that the vibrations of the *o*-carbaborane nucleus are hindered compared with the *m*-isomer both owing to the much more effective conjugation of the *o*-carbaborane fragment with the aromatic rings and due to steric effects. This feature is reflected in the relaxation processes in the carbaborane-containing polymers, the results of the study of which by various methods indicate an increase of the rigidity of the macrochain and an increase of the softening temperature on passing from *m*- to *o*-carbaborane-containing polyesters[51,52].

Ionic electrical conduction is mainly characteristic of carbaborane-containing polyesters, the conductivity of *o*-carbaborane-containing polyesters being higher by 1–2 orders of magnitude than the corresponding values for polyesters with *m*-carbaborane fragments[53].

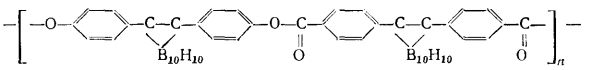
The structural-chemical transformations of *o*- and *m*-carbaborane-containing polyarylates on isothermal heating (225 to 325 °C) *in vacuo* in the presence of oxygen have been investigated[55]. It has been established that at a temperature as low as 225 °C processes involving the rupture of the ester linkage take place in the polymers with simultaneous changes in the carbaborane fragments (decrease of the number of B–H bonds and the appearance of the B–O–B linkages) and the formation of cross-linked structures. It has been shown that in the presence of oxygen the latter are formed owing to the interaction of the carbaborane fragments with oxygen, while *in vacuo* they result from the interaction with the oxygen-containing groups in the macromolecules.

In order to elucidate the influence of the quantitative content of *m*-carbaborane fragments on the thermal stability of polyarylates, a comparative study has been made of the thermal stabilities of polymers having the following structures[57]:



It has been established that the temperature of the onset of the decomposition of the test polymers (evolution of gaseous degradation products) *in vacuo* decreases from 375° to 320 °C as their content of *m*-carbaborane fragments increases. The different transformations of the *m*-carbaborane groups with evolution of hydrogen begin in all the polyesters at a temperature lower by 20–25 °C than the degradation of the main chain with formation of CO and CO_2. It is noteworthy that the weight loss by the polyester specimens at 700 °C diminishes from 34.7 to 19.5 wt.% with increase of their content of *m*-carbaborane fragments.

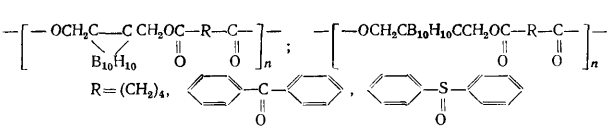
The structure of the involatile residues from the polyarylate having the structure



after its vacuum heat treatment in the temperature range 300–1200 °C has been studied by X-ray diffraction[56]. It was found that heating to 300 °C hardly induces any changes in the crystalline polymer specimen; under analogous conditions, an amorphous specimen becomes crystalline. An increase of the temperature to 400 °C leads to the complete disruption of the crystalline structure of the polyarylate and its conversion into the amorphous form. After heating at 500 °C, considerable chemical transformation occur in the polymer and an appreciable amount of H_3BO_3 is formed, indicating the interaction of the *o*-carbaborane groups and the products of their thermal transformations with the oxygen bound chemically in the polymer. At 600 °C the structure of the polyarylate with *o*-carbaborane fragments is fully disrupted and a dense network structure with strong B–B and B–O bonds is produced. Treatment at 700 °C leads to the appearance of a small number of graphite blocks; subsequent heat treatment of the polymer up to 1000 °C is hardly reflected in the structure and the mass of the specimens changes by only 5–8% under these conditions.

From their investigation, the authors[56] concluded that the main difference between the *o*-carbaborane-containing polyarylates and their normal analogues consists in the displacement of the temperature of the extensive decomposition and the rearrangement of the initial structure into the region of high temperatures and also in a specific interaction of the *o*-carbaborane fragments or the products of their thermal transformations with the chemically bound oxygen.

However, in the case of thermally less stable structures, for example, polyesters with aliphatic fragments having the structure



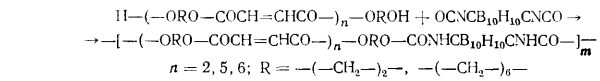
the presence of carbaborane groups does not affect the mechanism of the degradation of the polymers in the temperature range 300–420 °C.[58] The polyesters of aromatic dicarboxylic acids are stable on heating to 350 °C and those of

adipic acid are stable up to 250 °C. The thermal degradation of these polymers in the above temperature range proceeds without change in the carbaborane fragments via the mechanism usual for organic polymers.

There exist data concerning the use of *o*-carbaborane-containing polyarylates as binders for the formation of thermoplastic and thermostable self-lubricating materials[59] and for the preparation of negative photoresistors[60]. Furthermore, the VK-28 epoxide adhesive, which hardens at 150–200 °C and forms adhesive junctions between steel specimens having a shear resistance of 100–140 kg cm^{-2} at 20 °C and 80–90 kg cm^{-2} at 250 °C, has been devised on the basis of carbaborane polyethers[42,61].

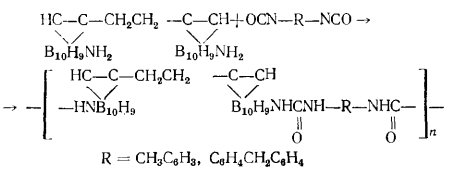
2. Polyurethanes and Polyureas

The synthesis of *m*-carbaborane-containing unsaturated polyurethanes, formed by the interaction of unsaturated oligoesters with *m*-carbaboranylene di-isocyanate in accordance with the scheme[62]



has been described. The reaction is almost quantitative and does not involve the formation of volatile products. The polymers obtained are colourless rubber-like substances which are readily soluble in chloroform, tetrahydrofuran, acetone, benzene, and styrene and are insoluble in alcohol, ether, and hexane. They exhibit an effective adhesion to metallic surfaces and are capable of being hardened by styrene at 80 °C. According to thermogravimetric data obtained in air, the weight loss by the hardened polyurethane specimens is 5% at 340–350 °C (for a heating rate of 4.5 K min^{-1}). An adhesive composition, which hardens at room temperature after 6 h or at 85 °C after 2 h is effective at temperatures ranging from −60° to +150 °C, and can be used to join articles made of metals, plastics, ceramics, and glass, has been obtained on the basis of the *m*-carbaborane-containing polyurethanes synthesised[63]. In addition, the VK-20 hot-hardening adhesive, which is a polyurethane composition modified by a carbaborane-containing compound, has been described[42,64]. The adhesive junctions based on it are effective for 500 h at 350–400 °C and briefly at 800 °C. The VK-20 M adhesive, whose composition is analogous to that of the VK-20 adhesive, contains a catalyst which makes it possible to harden it at room temperature[42].

o-Carbaborane-containing polyureas have been obtained by the interaction of 1,2-di(*B*-amino-*o*-carbaboranyl)ethane with di-isocyanate in tetrahydrofuran at 18–25 °C in accordance with the scheme[65]

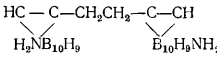


These polymers soften at 195–200 °C, begin to decompose at 240–250 °C, and their coke residues after heat treatment in air at 800 °C amount to 90–92%.

3. Polyamides

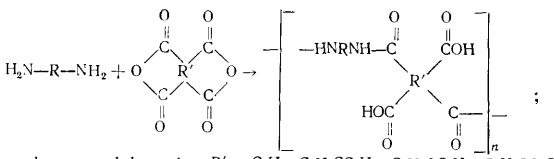
In the publications of the last decade comparatively little attention has been devoted to the synthesis of new carbaborane-containing polyamides[66–68], but a whole series of studies have been undertaken to investigate various properties of polyamides described previously[69–83].

A diamine in which the amino-groups were attached to a boron atom of the carbaborane nucleus and not to a carbon atom was first used for the synthesis of carbaborane-containing polyamides[66]:



Polyamides stable on heating in air to 320–330 °C were obtained by the polycondensation of this diamine with aromatic dicarboxylic acid dichlorides.

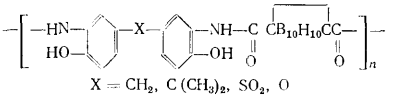
The synthesis and properties of polyamidoacids, obtained by the reaction of *m*- or *p*-carbaboranylenediamines with tetracarboxylic acid dianhydrides, has been reported[67]:



R = *m*-carbaboranylene or *p*-carbaboranylene; R′ — C_6H_2, $C_6H_3CC_6H_3$, $C_6H_3OC_6H_3$, $C_6H_3SO_2C_6H_3$.

All the *m*- and *p*-carbaborane-containing polyamidoacids are light coloured powders with η_{int} = 0.1–0.5 dl g^{-1}, which are readily soluble in the majority of organic solvents. *p*-Carbaborane-containing polyamidoacids hardly undergo a change in their viscosity characteristics on storage in the dry stage and in solution (in *N*-methylpyrrolidinone). Polyamidoacids with *m*-carbaborane fragments gradually decompose; their viscosity characteristics (the value of η_{int}) decrease from 0.35 to 0.20 dl g^{-1} after storage for a month.

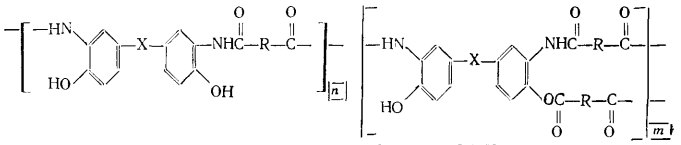
A study has been published[68] in which *p*-carbaborane-containing polyhydroxyamides having the structure



were obtained by analogy with the *m*-carbaborane-containing polyhydroxyamides described previously[1]. The structure of the *p*-carbaborane-containing polymers has been confirmed by elemental analysis and by comparing their infrared spectra with those of a model compound—the 1,12-di(*o*-hydroxyphenylamide) of *p*-carbaboranedicarboxylic acid. In contrast to the infusible *m*-carbaborane-containing polyhydroxyamides, the *p*-carbaborane-containing polyhydroxyamides soften in the range 220–270 °C and their molecular weights are 9000 to 10 000. As regards chemical stability, polyhydroxyamides with *p*-carbaborane fragments are analogous to the corresponding *m*-derivatives.

It has been noted[69] that, depending on the conditions in the formation of *m*- and *p*-carbaborane-containing polyhydroxyamides (depending on the ratio of the starting materials, the nature of the solvent, and other factors determining the course of the polycondensation process), their

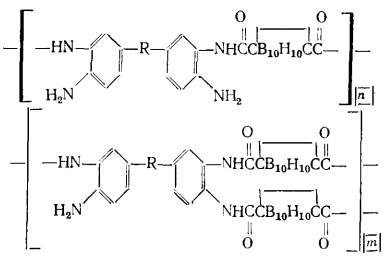
macromolecules can incorporate both linear and branches units:



R = *m*-carbaboranylene or *p*-carbaboranylene; X = CH_2, $C(CH_3)_2$, SO_2, O .

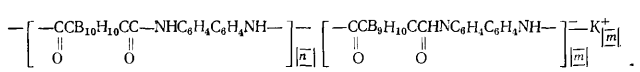
Their ratio $n : m$ varies from 1 : 0 to 0 : 1. The degree of heterounit structure in these polymers has been estimated quantitatively with the aid of infrared spectroscopy[69].

The relation between certain properties of *p*-carbaborane containing polyaminoamides and the structure of their macromolecules has been investigated[70]:



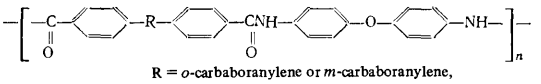
It was established that, as the degree of heterounit structure of the polyamides ($n : m$) varies from 0.9 : 1 to 1 : 9, the degree of their 'swellability' in tetrahydrofuran increases from 55% to infinity (i.e. the polymers become soluble) and the interchain distance in the polymer diminishes from 5.8 to 5.4 Å.

In the study of the chemical stabilities of the *m*-carbaborane-containing polyamides obtained previously it was observed that the *m*-carbaborane fragments are cleaved to the dicarbaundecaborate anion by dimethylformamide on heating to 100 °C or by alcoholic alkali in solution in tetrahydrofuran to form polyamides having the following structure[71]:



The dicarbaundecaborate fragments in these polyamides were determined quantitatively by ^{1}H NMR [72] and it was shown that the heterounit polyamide in which the numbers of the *m*-carbaborane and dicarbaundecaborate fragments are approximately equal ($n \cong m$) differs in a number of features from the polyamide containing only *m*-carbaborane groups ($m = 0$). Thus, in contrast to the latter, the heterounit polyamide does not dissolve in tetrahydrofuran, but is readily soluble in dimethyl sulphoxide and methanol, and transparent films of the polymer can be obtained from these solutions. The presence of dicarbaundecaborate fragments in the macromolecule greatly reduces the chemical and thermal stabilities of the polymer. Thus the viscosity of the heterounit polyamide decreases from 1.20 to 0.7 dl g^{-1} in boiling water after 3 h, while under the influence of dry HCl it diminishes from 1.20 to 0.3 dl g^{-1} in 1 h. The initial *m*-carbaborane-containing polyamide remains unchanged in both cases. The temperature of the onset of evolution of hydrogen from the heterounit polyamide is 80 °C, while that for the *m*-carbaborane-containing polymer is 200 °C.[71]

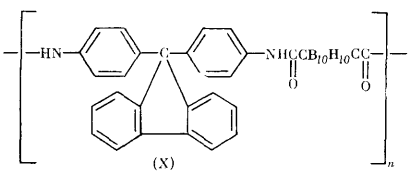
The electrophysical properties of *o*- and *m*-carbaborane-containing polyamides having the structure



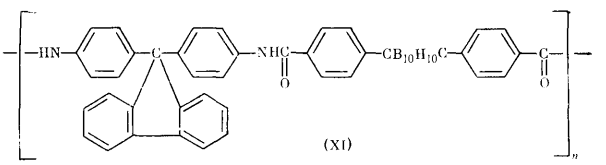
R = *o*-carbaboranylene or *m*-carbaboranylene,

have been investigated. It was shown that the replacement of the *o*-carbaborane fragment in the polyamides, as in the carbaborane-containing polyarylates, by the *m*-carbaborane fragment diminishes the rigidity of the macrochains[73].

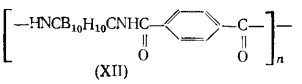
The study of the structural transformations of polyamides having the structures



(X)



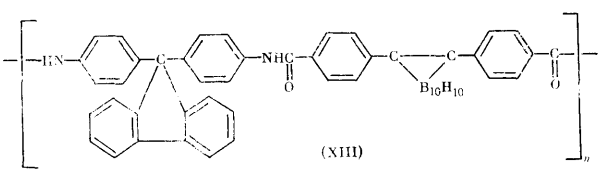
(XI)



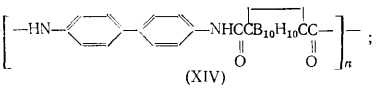
(XII)

at 100–350 °C *in vacuo* in an atmosphere of oxygen and water vapour established that in the above temperature range their macromolecules undergo simultaneously cross-linking and cleavage[74]. The branching and cross-linking processes predominate in the polyamide (XI), while chain dissociation as a consequence of the cleavage of the *m*-carbaborane fragments predominates in the polyamides (X) and (XII).

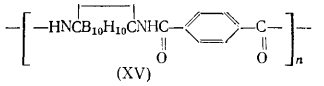
Questions concerning the degradation of the *m*-carbaborane-containing polyamides (X)–(XII) as well as polyamides with *o*- and *p*-carbaborane fragments having the structure



(XIII)



(XIV)



(XV)

in vacuo and in an atmosphere of oxygen and water vapour at 200–800 °C have been considered in detail in a review by Korshak et al.[6] The study of carbaborane-containing polyamides of this kind revealed the influence on the thermal stability of the polymers not only of the isomerism of the carbaborane group but also of the chemical nature of their substituents, in particular the influence on the stability of the carbaborane nucleus by nucleophilic and electrophilic groups such as the carbonyl, phenyl, and amide groups.

Korshak et al.[6] established that the isomerism of carbaborane influences significantly the stability of polyamides *in vacuo*. Whereas the breakdown of the *o*- and *m*-carbaborane fragments is the main degradation reaction in the polyamides (X)–(XIII), the amide groups becoming resistant to homolytic and heterolytic decomposition reactions, in the *p*-carbaborane-containing polyamides the NH–CO linkages are broken.

The isomeric *m*- and *p*-carbaborane-containing polyhydroxyamides have also significantly different thermal stabilities[68].

The antifriction properties of the *p*-carbaborane-containing polyamide (XIV) and its *m*-isomeric analogue have been investigated in the temperature range 250–450 °C.[75] On the basis of the results, the authors concluded that the hydrogen formed in large amounts on decomposition of *m*-carbaborane-containing polyamides creates a reducing medium between the surfaces involved in friction, which leads to the inhibition of the oxidative processes occurring at high temperatures. This is to a large extent responsible for the improvement of the lubricating properties of the antifriction plastics based on *m*-carbaborane-containing polyamides compared with the *p*-carbaborane-containing polyamides (a smaller amount of hydrogen is evolved from the latter in the experimental temperature range) and compared with polyamides without carbaborane fragments (these hardly evolve hydrogen at the above temperatures).

A series of studies in which the polyamides of *m*-carbaboranedicarboxylic acid were used as stabilisers against the thermal and thermo-oxidative degradation of aromatic cardo-polyamides[76–80] and polyphenylquinoxalines[81] have been published. It was established that, both *in vacuo* and in oxygen, the polyamides of *m*-carbaboranedicarboxylic acid are effective stabilisers of cardo-polyamides, which is reflected both in a considerable decrease of the rate of evolution of carbon oxides and in a decrease of the weight loss by the polymer specimens at 300–450 °C.[76,79] The authors suggest that the high thermal stability of specimens of aromatic cardo-polyamides to which 0.5 wt.% of the polyamide of *m*-carbaborane-dicarboxylic acid has been added is due to the appreciable weakening of the degradative processes and the formation during heat treatment of cross-linked structures containing the thermally stable B–N, B–C, and B–O bonds[82,83].

4. Poly-Schiff Bases

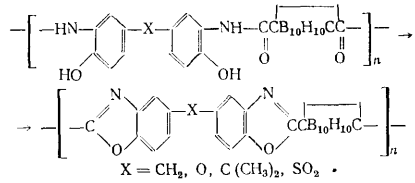
Only tentative data have been published about *m*- and *p*-carbaborane-containing poly-Schiff bases[84,85]. These polymers were first obtained by French investigators by the interaction of *m*- or *p*-carbaboranedialdehydes with various aromatic diamines in halogenated hydrocarbons, phenols, dioxan, and tetrahydrofuran in the presence of acceptors of the water involved, namely sodium and magnesium sulphates, calcium chloride, or molecular sieves. Polymers having the structure

$$H_2—[—NArN=CH—R—CH=]_n=O$$

(R = *m*-carbaboranylene or *p*-carbaboranylene; n = 5–1000), which are readily soluble and thermally stable, were obtained. They have been recommended for the manufacture of films, adhesives, and surface coatings.

5. Polyheterocycles

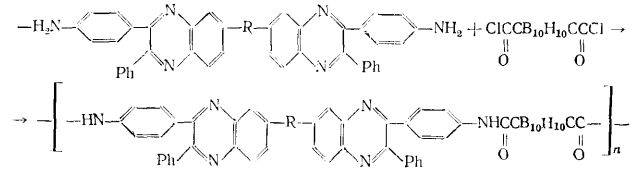
Recently Korshak and co-workers synthesised carbaborane-containing polybenzoxazoles and polyphenylquinoxalines which had not been described previously[86–88]. *p*-Carbaborane-containing polybenzoxazoles were obtained by the thermal or chemical (in polyphosphoric acid) cyclocondensation of the corresponding poly-*o*-hydroxyamides in accordance with the scheme[86,87]



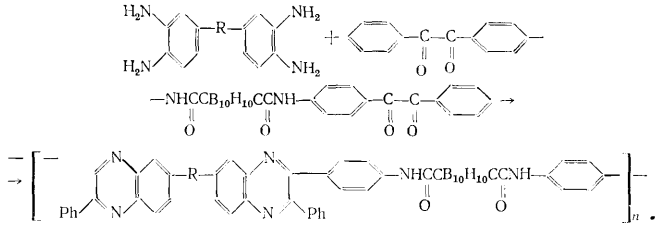
X = CH_2, O, $C(CH_3)_2$, SO_2 .

The structure of the polybenzoxazoles obtained was confirmed by elemental analysis and by comparing the infrared spectra of the polymers and model compounds. All the *p*-carbaborane-containing polybenzoxazoles are yellowish or pale-brown powders, which are amorphous (according to X-ray diffraction data) and soluble in amide solvents and in a tetrachlorethane–phenol mixture. The intrinsic viscosities of these polymers are 0.4–1.1 dl g^{-1}, their softening temperatures are in the range 290–360 °C, their decomposition temperatures are 400–550 °C, and their coke residue in air at 900 °C amounts to 80–98%. Polybenzoxazoles with *p*-carbaborane fragments are hydrolysed by hot water (η_{int}^{25} diminishes from 1.1 to 0.4 dl g^{-1} after boiling the polymer in water for 24 h).

m-Carbaborane-containing polyphenylquinoxalines have been synthesised in two ways[88]: 1) by the polycondensation of bis(aminophenylquinoxalines) with *m*-carbaboranedicarboxylic acid chloride in tetrahydrofuran at room temperature using triethylamine as the acceptor of the hydrogen chloride evolved:



2) by the interaction of aromatic tetramines with *m*-carbaborane-containing bis(α-diketone) at room temperature in *m*-cresol or in chlorinated hydrocarbons with added proton donors:

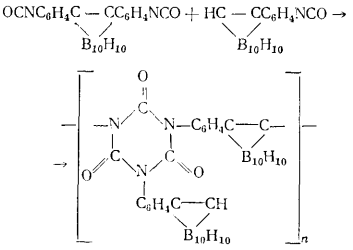


The use of mixtures of *m*-carbaboranedicarboxylic acid chloride with the chlorides of other dicarboxylic acids in various proportions in the first method of synthesis or of mixtures of bis(α-diketones) in the second method makes it possible to vary the content of the *m*-carbaborane fragments in the polymers and the properties of the latter in the required way. The *m*-carbaborane-containing polyphenylquinoxalines synthesised are fibrous or powdered products

with intrinsic viscosities in the range 0.8–2.2 dl g^{-1}. Depending on the quantitative content of the *m*-carbaborane groups in their macromolecules, the polymers soften in the temperature range 280–310 °C or begin to decompose, without softening, at ~400 °C. The carbon residue from the polymers after heat treatment in air at 800 °C amounts to 32–57%, while in an inert atmosphere it amounts to 70–80%. The solubilities of certain *m*-carbaborane-containing polyphenylquinoxalines in chloroform and tetrahydrofuran make it possible to obtain films with effective physicomechanical parameters from their 10% solutions.

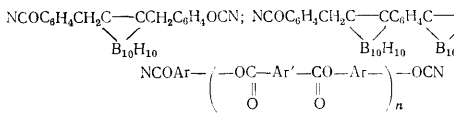
It is believed[88] that *m*-carbaborane-containing polyphenylquinoxalines are of undoubted interest for practical applications as heat-resistant and thermostable film materials, coatings, binders, fibres, etc.

There are reports in the patent literature concerning the synthesis of *o*- and *m*-carbaborane-containing polyisocyanurates, polycyanurate, and polymelamines[89–92]. *o*-Carbaborane-containing polyisocyanurates have been obtained by the polycyclotrimerisation of 1,2-di(isocyanatophenyl)-*o*-carbaborane with 1-isocyanatophenyl-*o*-carbaborane in a polar organic solvent (butyl acetate or dimethylformamide) or without solvent at 150–170 °C:[89]



Mixtures of various mono- and di-isocyanates have also been used instead of the *o*-carbaborane-containing monoisocyanates. Depending on the ratio of the starting materials, fusible soluble or infusible and insoluble polymers with enhanced thermal and thermal-oxidative stabilities were obtained.

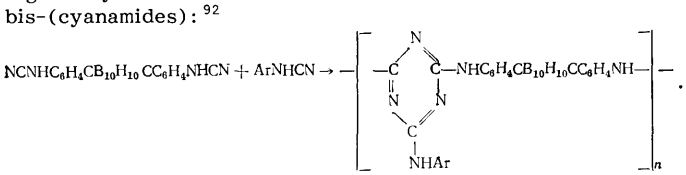
Polycyanurates with *o*- and *m*-carbaborane fragments have been obtained either by the polycyclotrimerisation of the *o*- and *m*-carbaborane derivatives[90,91]



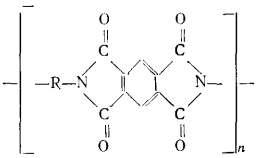
Ar = *o*-carbaboranylene, Ar′ = *o*- or *m*-carbaboranylene, and *n* = 1–20,

or by their copolymerisation with the monocyanate C_6H_5OCN. The temperature of the onset of decomposition of these polymers is 310–380 °C in air and 380–390 °C in an inert atmosphere, their specific impact strength reaches 30 kg cm^{-2}, their Brinell hardness is 1600 kg cm^{-2}, and their bending strength is 1500 kg cm^{-2}. The authors[90,91] suggested that the degradation of polycyanurates begins with the hydrolytic cleavage of the ester linkage and is accompanied by the subsequent decomposition of the triazine ring via both heterolytic and homolytic mechanisms.

The corresponding polymelamines have been synthesised by the polycyclotrimerisation of the *m*-carbaborane-containing bis(cyanamides) or their mixture with aromatic mono- and bis-(cyanamides):[92]



The thermal and chemical cyclodegradation of *m*- and *p*-carbaborane-containing polyamidoacids, which results in the formation of the polyimides having the following structure have been described[67]:



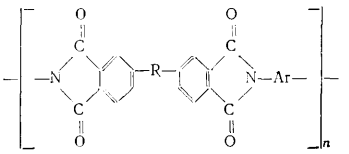
R = *m*-carbaboranylene or *p*-carbaboranylene.

It has been established that the formation of *m*-carbaborane-containing polyimides is accompanied by the conversion of the *m*-carbaborane fragments into dicarbaundecaborate fragments, while the conversion of polyamidoacids with *p*-carbaborane groups into a polyimide takes place without the cleavage of the *p*-carbaborane nucleus.

All the polyimides obtained in this way are soluble in amide solvents and the intrinsic viscosities η_{int} = 0.15–0.40 dl g^{-1} have been obtained for them. The polyimides with *m*-carbaborane fragments do not soften and begin to be oxidised in air at 250 °C, while those with *p*-carbaborane fragments soften at 400–450 °C with decomposition. The carbon residues from these polymers after heating in air up to 800 °C amount to 79–100%.

The study of the thermal degradation of these polymers in the temperature range 100–600 °C established that the introduction of *m*-carbaborane fragments into the polyimide macromolecule reduces the rate of the homolytic and heterolytic decompositions of the rings to a greater extent than the introduction of *p*-carbaborane groups[93].

The electrophysical properties and molecular mobilities of *o*- and *m*-carbaborane-containing polyimides having the following structure have been studied in detail[94,95]:



R = *m*-carbaboranylene or *o*-carbaboranylene.

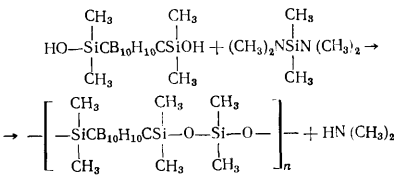
The study of the pyrolysis of these polyimides at 1000 °C in an inert medium and in air established that the diphenyl-*o*-carbaborane or diphenyl-*m*-carbaborane fragments with the adjoining imide rings are subjected to homolytic decompositions to the greatest extent and their primary decomposition products can be H_2 (from carbaborane fragments), carbon monoxide (from the imide ring), benzene, and mono- and di-phenyl-*o*- or -*m*-carbaboranes[96]. The yield of carbon from the *o*- and *m*-carbaborane-containing polyimides in an inert atmosphere is 93–95% on heating to 900 °C.

6. Polysiloxanes and Polysilazanes

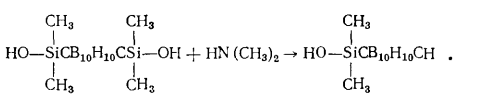
The studies in the field of new methods of synthesis of *m*-carbaborane-containing polysiloxanes of the type of Dexsil and the studies of their properties continue to develop vigorously. The difficulties in the synthesis and vulcanisation of these polymers, in which improved thermal stability is combined with elasticity, hinder their practical application[97].

In the methods of synthesis of Dexsils used previously[1] the difficulties were associated with the employment of iron(II) chloride as the catalyst of the condensation of *m*-carbaborane-containing chlorosilane and alkoxysilane, which induced premature structure formation and prevented the formation of

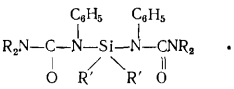
linear polymers. A new method of synthesis of linear Dexsils with a molecular weight of ~18 000, based on the condensation of an *m*-carbaborane-conaining disilanol with a reactive silane, for example bis(*N*,*N*-dimethylamino)dimethylsilane or bis(*N*,*N*-dimethylcarbamato)dimethylsilane, under mild conditions has been described[97]:



The formation of Dexsils with higher molecular weights by both procedures is prevented by the occurrence of the side reaction



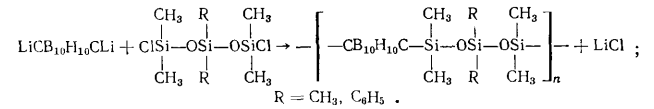
Dexsils with molecular weights > 25 000 have been synthesised using stable bisureidosilanes as the reactive silanes[97–99]:



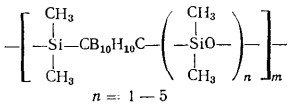
With increase of the molecular weight of Dexsils to 283 000, there is a sharp improvement of their elastomeric properties. Thus polymers with molecular weights of 50 000, 150 000, and 283 000 have tensile strengths of 7.0, 7.2, and 23 kg cm^{-2} and relative elongations of 5, 60, and 700% respectively.

A new method of synthesis of Dexsils[97–99] facilitates its modification. For example, by employing a certain amount of bis(ureido)diphenylsilane or bis(ureido)methylphenylsilane in the bis(ureido)silane mixture during the synthesis, one can introduce phenyl groups into Dexsils in order to improve their thermo-oxidative stability[98]. Trifluoropropyl groups are introduced similary into Dexsils in order to improve their resistance to the action of solvents[100].

American investigators proposed another very convenient method of synthesis of Dexsils directly from *m*-carbaborane[101]:



However, the molecular weights of the polymers thus obtained are low. Studies on the influence of the length of the siloxane fragment on the thermal characteristics of poly-*m*-carbaboranylenesiloxanes having the structure



are being continued[102,103]. Their results confirm the earlier conclusion that, with increase of the length of *n* of the siloxane fragment from 1 to 5, the glass points of the polymer gradually diminish from 25° to −88° and the weight losses by the polymer specimens after heat treatment at 800 °C in argon increase greatly.

The thermal, thermo-oxidative, and hydrolytic stabilities of high-molecular-weight poly-*m*-carbaboranylenesiloxanes have been studied in detail[103–105]. It was established[104] that the main transformations are undergone by the polymers in the temperature ranges 240–310 °C and 450–550 °C. A virtually complete loss of solubility of the polymer without change in the mass of its specimens is characteristic of the first temperature range, while only a change in the mass of the specimens, amounting to 3–6% in argon and 1–3% in air, is characteristic of the second range.

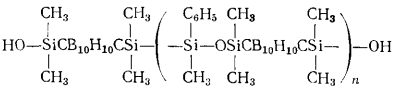
It has been shown that the thermal degradation of poly-*m*-carbaboranylenesiloxanes involves two competing processes: the degradation of the main chain, which results in the formation of oligomeric products, and the dissociation of the Si–C and C–H bonds accompanied by the evolution of CH_4 and H_2 and leading to structure formation[103]. The replacement of one or several methyl groups by phenyl groups activates the structure formation processes and diminishes the weight losses by the polymer specimens. The thermo-oxidative stability of poly-*m*-carbaboranylenesiloxanes greatly increases in the presence of Fe_2O_3.[106]

A characteristic feature of the thermal degradation of poly-*m*-carbaboranylenesiloxanes is an insignificant content of cyclic oligosiloxanes in the decomposition products[105]. It has been suggested[105] that the large bulk of the *m*-carbaborane groups prevents the formation of a helical form of the macromolecule and hinders thereby the decyclopolymerisation of the *m*-carbaborane-containing polysiloxanes. It has also been noted that the introduction of *m*-carbaborane fragments into the main chain of siloxane polymers reduces their hydrolytic stability as a result of of the appearance of the hydrolytically weak Si–$C_{carbaborane}$ linkage in these substances[104].

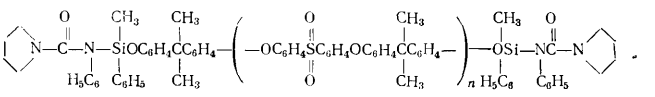
A method for the quantitative determination of the degree of branching of poly-*m*-carbaboranylenemethylphenylsiloxane, obtained in the presence of catalytic amounts of $FeCl_2$, has been proposed[107].

Poly-*m*-carbaboranylenesiloxanes tend to crystallise, which greatly impairs their elastomeric properties[108]. In order to diminish the crystallinity of these polymers, it has been suggested[108] that some of the *m*-carbaborane fragments be replaced by *p*-carbaborane fragments or that dimethylsiloxane units be replaced by diphenylsiloxane units. It was established that the introduction of 30 mole % of *p*-carbaborane or 33 mole % of diphenylsiloxane fragments into poly-*m*-carbaboranylenesiloxanes is sufficient for the formation of a fully amorphous polymer.

A new thermoplastic elastomeric block copolymer with $M \cong 10^6$ has been obtained by the reaction of poly-*m*-carbaboranylenesiloxane having terminal OH groups (molecular weights 45 560), i.e.

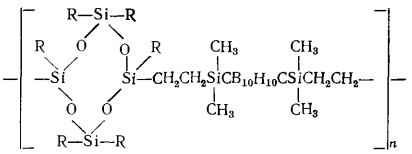


with the polysulphone (molecular weight 6020) [109]



It was shown that this block copolymer has two glass points (−27° and 165 °C), which correspond to the elastic (poly-*m*-carbaboranylenesiloxane) and rigid (polysulphone) blocks. According to thermogravimetric data, the block copolymer is stable up to 400 °C and is usable in the range from −40 °C to >300 °C. Polyimides, polyesters, poly(phenylene sulphides), and polybenzimidazoles can also be used for the preparation of the block copolymers instead of the polysulphone[110].

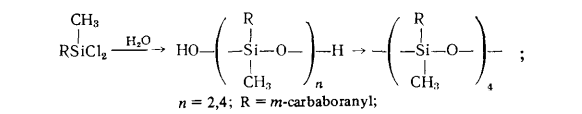
There exist patent data concerning the synthesis of linear *m*-carbaboranylenesiloxane oligomers having the following structure[111]:



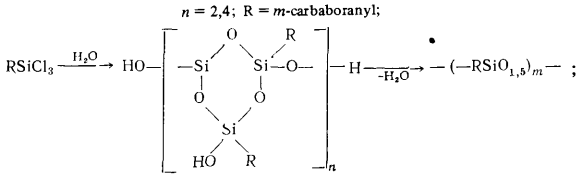
R = alkyl or aryl and n = 3-5.

These are formed when equimolar amounts of divinylorganocyclosiloxane and di(hydroxymethyl)-*m*-carbaborane interact at 50–200 °C in the presence of a hydrosilylation catalyst. When trivinylorganocyclosiloxane is used, branched oligomers are obtained[112]. All the oligomers synthesised in this way are transparent viscous liquids with $M \cong 2000$, which are readily soluble in aromatic hydrocarbons, ethers, and esters. The authors[112] recommend their use as thermostable rubbers and hermetic seals. The temperature of the onset of the thermo-oxidative degradation of the oligomers in air is ~400 °C. Infrared spectroscopic data have shown that the oligomers are synthesised solely as a result of the hydride addition reaction with retention of the structures of the initial compounds in the oligomers.

Oligomers with silanol groups have been obtained by the hydrolytic polycondensation of *m*-carbaboranylmethylorganochlorosilanes. Compounds with cyclic or cyclic-three-dimensional structures are formed from these substances at 250 °C:[113]



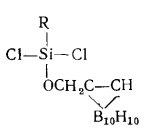
n = 2,4; R = *m*-carbaboranyl;



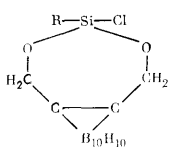
n = 2,3; m = 18, 24 .

The hardening of phenol-organosilicon oligomers by *N*,*N*-di(hydroxymethyl)aminophenol-*o*-carbaborane has been studied[114] and it has been found that the polymers hardened in this way exhibit a high thermal stability and heat resistance, while materials based on them possess improved dielectric properties.

Oligomeric organosilazanes containing *o*-carbaborane-fragments in the main or side chains in their molecules were synthesised for the first time by the ammonolysis of *o*-carbaboranylmethoxy(organo)dichlorosilanes



or *o*-carbaboranylenedimethoxy(organo)chlorosilanes



R = CH_3, C_6H_5, $CH{=}CH_2$

or by the co-ammonolysis of their mixture with organochlorosilanes having the formula R_mSiCl_{3-m}.[115,116] The *o*-carbaborane-containing oligo-organosiloxanes obtained have been recommended as hardening and modifying agents for polyphenylenes[117].

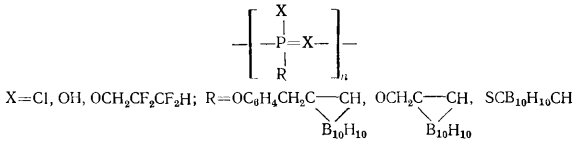
The practical value of poly-*m*-carbaboranylenesiloxanes, in which a high thermal stability (up to 500 °C) is combined with effective fire resistance (oxygen index 62), has been noted in a review[118]. These polymers have found extensive applications as the liquid phases in gas chromatography for the separation of organosilicon and organic substances[119] and for the analysis of polycyclic aromatic hydrocarbons at 20–450 °C.[120]

Adhesive compositions, capable of being used for a long time (up to 2000 h) at 600 °C and of withstanding brief exposures to a temperature of 1200 °C, have been created on the basis of *m*-carbaborane-containing polysiloxanes[42,121]. These adhesives are designed for the glueing of semiconducting materials to metals and silicate glasses in electrovacuum devices.

Poly-*m*-carbaboranylenesiloxanes are used as coatings for conducting wires and other articles capable of withstanding a temperature of ~300 °C [118,122] and also as lubricating materials in constructions subjected to irradiation at high temperatures[123].

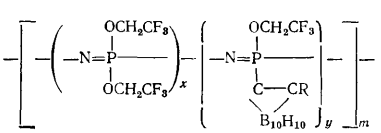
7. Polyphosphazenes

In order to improve the thermal stability of polyphosphazenes, Korshak and co-workers attempted to introduce *o*- and *m*-carbaboranyl groups into these polymers; as a result, *o*- and *m*-carbaborane-containing polyphosphazenes



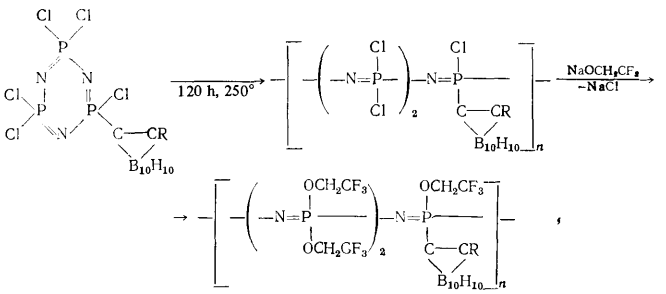
were obtained for the first time and characterised[124,125]. It was shown that, when polydichlorophosphazenes react with monolithio-derivatives of the corresponding *o*-carbaboranes or with monomercapto-*m*-carbaborane in solution in tetrahydrofuran, the maximum degree of substitution of chlorine by *o*- or *m*-carbaboranyl groups does not exceed 50%. The polymers obtained are white or pale-yellow powders with intrinsic viscosities ranging from 0.15 to 3.00 dl g^{-1}. Their chemical and thermal stabilities are determined by the character of the groups surrounding the main polymer chain. The softening temperatures of these polymers are therefore in the range 90–270 °C and the carbon residue after heat treatment in helium at 900 °C is 26–100%.

Somewhat later Allcock and co-workers[126–128] described *o*-carbaborane-containing polyphosphazenes having the structure

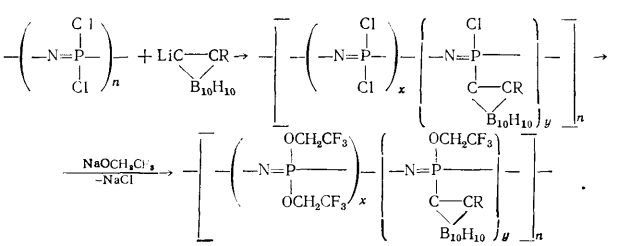


R = CH_3, C_6H_5 .

These polymers were obtained by two methods: either by the polymerisation of the corresponding mono-*o*-carbaboranyl-pentachlorocyclotriphosphazene in sealed tubes with subsequent substitution of chlorine atoms by CF_3CH_2O groups:



or by the interaction of polydichlorophosphazene (molecular weight 10^4–10^6) with monolithio-*o*-carbaborane:



The molecular weights of some of the *o*-carbaborane-containing polyphosphazenes obtained in this way reached 10^5 and the carbon residue in an inert atmosphere at 1000 °C was 56.5%. The authors[128] recommend *o*-carbaborane-containing polyphosphazenes for use as thermostable thermally insulating materials.

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Thus the literature data published in recent years permit the conclusion that carbaborane-containing polymers continue to attract the attention of investigators. The study of the properties of polymers with carbaborane fragments, their modification, and the search for new, simpler methods of synthesis of polymers showing the greatest promise in practical applications are of special interest.

As regards the prospects for the further development of the chemistry of carbaborane-containing polymers, one can suppose that, in view of the high cost of the starting materials, the amount of these polymers manufactured will not be great; nevertheless, in view of their unique properties, they will probably become in future some of the most important of polymeric materials.

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Order of Lenin Nesmeyanov
Institute of Organoelemental
Compounds,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 135-175 (1984) U.D.C. 541.6

The Mechanism and Kinetics of the Polymerisation of Conjugated Diacetylenes. The Physical Properties of Polydiacetylenes

G.A.Vinogradov

The mechanisms of the polymerisation of disubstituted conjugated diacetylenes initiated in different ways are examined as are the factors influencing the polymerisation kinetics, the yield of the polymer, and the molecular weight distribution and the structure of the final product. Various physical properties of the most highly investigated polydiacetylenes are discussed: optical (including thermo- and solvato-chromism), non-linear optical, paramagnetic, electro-physicalm mechanical, etc. properties. The possible practical applications of polydiacetylenes are indicated.
The bibliography includes 289 references.

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I. INTRODUCTION

In polymer chemistry, the preparation of polymeric single crystals of macroscopic size has been of interest for a long time. It has been shown[1] that at the present time this problem can be solved for polymers with conjugated bonds only in the case of polydiacetylenes—polymers based on disubstituted diacetylenes (DA) with conjugated triple bonds having the structure $R-C\equiv C-C\equiv C-R'$ (in the present review DA will be understood only as diacetylenes having this structure).

During the comparatively short time that has elapsed since the publication by Wegner in 1969 of the first communication on this topic, it has been possible to synthesise several hundreds of DA with substituents of various types, and in many cases polymerise them with the formation of crystals and multilayers having different kinds of morphology. The materials obtained have many interesting properties which determine their possible practical applications (for example, non-linear optical properties, thermo- and solvato-chromism, high mobility of current carriers, high mechanical strength, thermal stability, etc.). Furthermore, the study of DA, of the mechanism and kinetics of their polymerisation, and of the relation between the electronic and molecular structures and the properties of the polymer help in the solution of many general problems of the chemistry and physics of polyconjugated systems whose investigation has been in most cases complicated by their structural and molecular inhomogeneity. In this sense polydiacetylenes (PDA) provide a unique opportunity, as model objects, for the investigation of the general characteristics of polyconjugated systems, since the specimen always represents a set of fairly long macromolecules having the same conformation. Certain PDA are soluble which makes it possible to study their equilibrium properties under conditions independent of external molecular stresses.

Only those DA which in the monomeric phase give rise to single crystals or mono- or multi-layers and polymerise subsequently with retention of the topological correspondence between the molecular structures of the monomeric and polymeric phases will be considered in the present review. The review is devoted mainly to questions of the kinetics and mechanism of the polymerisation of DA, the relation between the structure of PDA and their physical properties (optical, mechanical, and electrophysical) and their practical applications; the methods of synthesis of the initial DA will not be considered. In the foreign literature there are a number of reviews devoted to various questions of the synthesis and physical properties of DA and PDA[2-12]†. This review reflects the latest advances in the study of the physical properties of PDA. In those cases where there is no unanimous view concerning some problems, the alternative approaches are described.

II. PRINCIPLES OF TOPOCHEMICAL POLYMERISATION

The solid-phase polymerisation of DA belongs to the class of topochemical reactions. According to Wegner's definition[2,11], topochemical polymerisation is understood as a non-diffusional conversion of a monomer single crystal into the corresponding polymer single crystal in which the mass centres of the monomeric units retain their initial crystallographic positions and the symmetry of the monomeric units in the monomer and polymer single crystals remains the same. The polymerisation reaction of DA, which is in essence a 1,4-*trans*-addition reaction, is achieved as a result of specific rotations of the monomeric units relative to the positions of their centres of mass, is determined by

† In addition, during the preparation of this article for the press, the following reviews were published: D.Bloor, Mol. Cryst.Liq.Cryst., 1983, **93**, 183; D.Bloor, in "Developments in Crystalline Polymers - 1", (Edited by D.C.Bassett), Applied Sci.Publ., London, 1982, p.151.

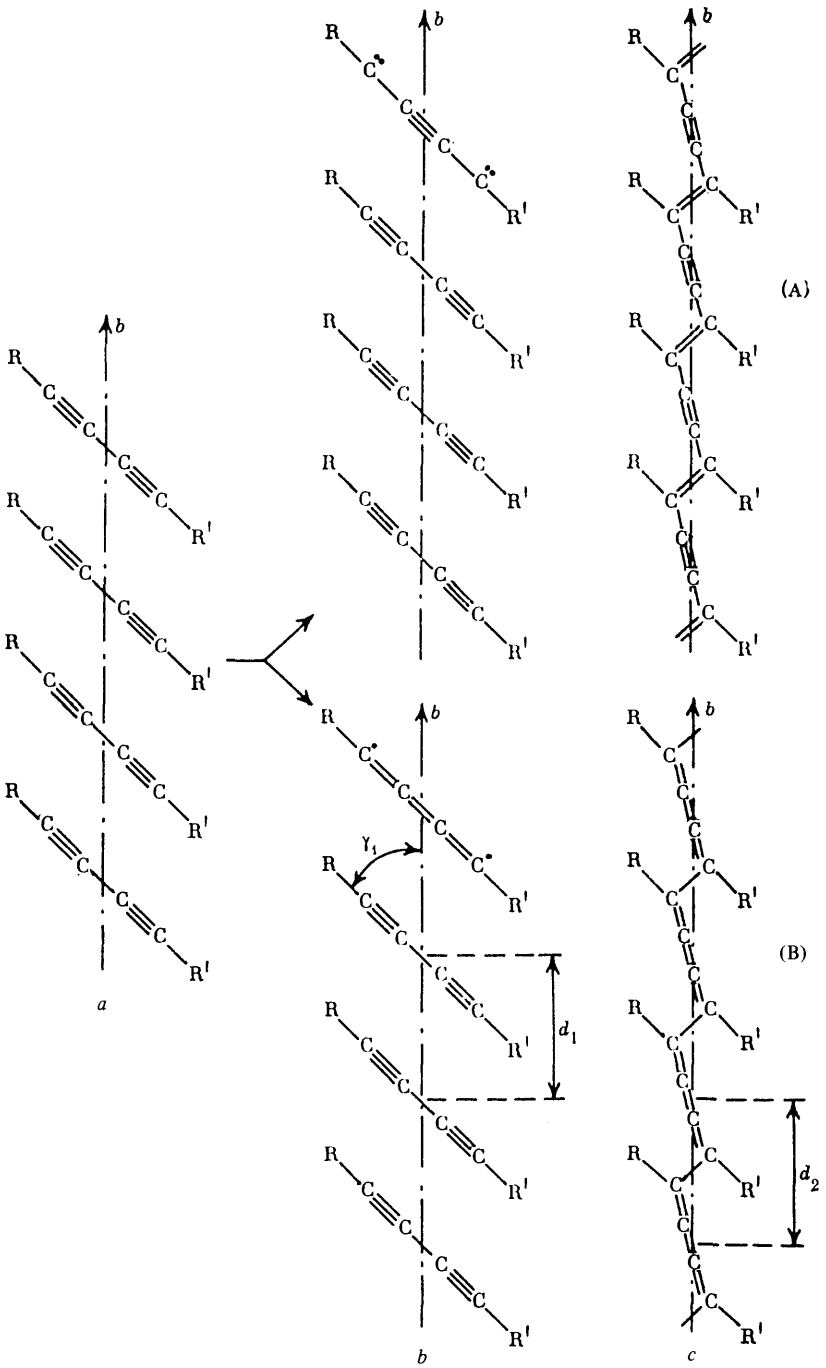


Figure 1. Schematic illustration of the topochemical polymerisation of DA: [2] *a*) arrangement of DA monomers in the single crystal; *b*) the structure of the initiating species in the carbene (above) and radical (below) initiation; *c*) PDA can exist as a function of type of initiation and structure factors in the enyne (A) or butatriene (B) mesomeric forms; *d*) axis of polymer chain.

the packing of the monomer in the crystal lattice, and proceeds without the formation of side products (Fig.1). Such stereospecific polymerisation results in the formation of a stereoregular polymer with a linear disposition of the macromolecules and with a small number of defects; in a number of instances the length of the polymer chain is comparable to the dimensions of the single crystal.

It has been shown by the topographic method using synchrotron radiation# that the solid phase polymerisation of diacetylenes is a true topochemical polymerisation, which takes place in the undeformed lattice of the monomer single

See M.Dudley, J.N.Sherwood, D.J.Ando, and D.Bloor, Mol.Cryst.Liq.Cryst., 1983, **93**, 223.

crystal in the absence of defects, in contrast to the other known solid-phase reactions, which can occur only in the vicinity of defects, dislocations, and admixtures.

The specific requirements which must be met for the occurrence of a topochemical reaction have been formulated by Baughman[10,13,14], who proposed several criteria whose fulfilment is necessary for the occurrence of such polymerisation reactions.

1. The criterion of minimum displacements states that the actual reaction pathway must be one in which the smallest mean square displacements of atoms take place. If this criterion for the four carbon atoms of the monomeric DA unit involved in the transition from the monomer to the polymeric phase is defined by the expression

$$R = \left\{\sum_{i=1}^{4} [(x_i, y_i) - (x_i', y_i')]^2\right\}^{1/2},$$

where x_i, y_i, x_i', and y_i' are the coordinates of the atoms in the monomeric and polymeric phases, then, according to Baughman, only those DA for which R is less than ~ 1.08 Å on passing from the monomer to the polymer are reactive.

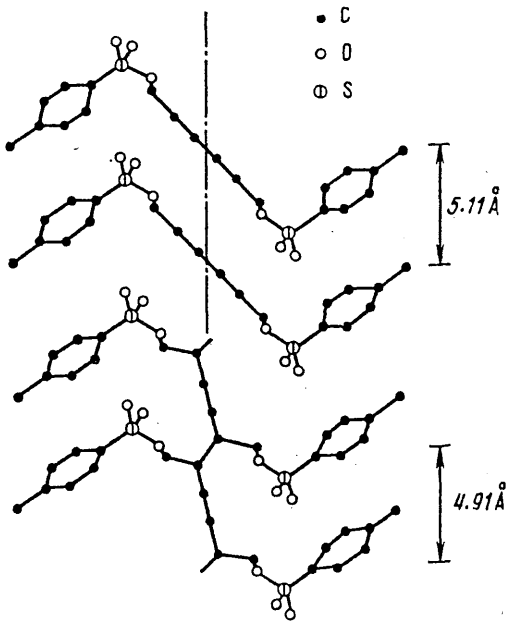


Figure 2. Projection of the crystal structure of TS (above) and poly-TS (below) onto the plane coinciding with the polymer skeleton[2].

As a rule the angle $\gamma_1 \cong 45°$ for the reactive DA and the relative lattice contraction $(d_1 - d_2)/d_2$ in the polymerisation reaction should not exceed approximately 0.1 (Fig.1), although there are exceptions to this empirical rule[2]. Fig.2 illustrates the changes in the geometrical disposition of the atoms of the monomeric TS unit (see Table 1 below) on passing from the monomer to the polymer. Evidently these changes are indeed small and reflect the rotation of the diacetylene group and the slight displacement and rotation of the benzene rings[2]. According to the minimum displacements criterion, the contribution of the lattice to the activation energy for the polymerisation reaction increases monotonically with increase of the mean square displacement of the atoms necessary for the occurrence of the reaction.

2. The group-theoretical criterion according to which the following conditions must be fulfilled for the reaction pathway to be unique: (a) the symmetry point group of the monomer must be a possible symmetry point group of the monomeric unit in the polymer and (b) the symmetry space group linking the reacting monomers must be a possible symmetry element between the corresponding monomeric units in the polymer chain. In other words, on passing from the monomer to the polymer, the degree of symmetry (point and space symmetry) must not decrease, i.e. during the reaction time all the crystallographic symmetry elements of the monomeric phase must be retained.

3. The criterion of the uniqueness of the phase transformation, which states that the polymer formed must be incorporated in the monomer matrix in the form of a solid solution for all degrees of conversion of the monomer. According to the last requirement, the monomeric and polymeric phases must be in equilibrium whatever the degree of conversion of the monomer[15].

The available literature data concerning unsuccessful attempts to polymerise a particular DA or the reported impossibility to attain 100% conversion of the monomer in the polymerisation reaction indicate the failure of at least one of the above criteria. Evidently the requirements enumerated impose very severe limitations on the size and interaction of the substituents. The role of the latter in topochemical polymerisation is great and reduces to the following[16]: the substituents control the packing of the monomer; they exert a steric influence on the reactivity, determining the unique reaction pathway; the interaction of the substituents controls the changes in the geometrical dimensions of the crystal lattice during polymerisation; they "soften" the mechanical stresses arising in the course of polymerisation owing to the incompatibility of the crystal lattice parameters of the monomer and the polymer. The specific requirements imposed on the substituents in the DA molecule are that as a rule they must have either a high dipole moment or the capacity to form intramolecular or intermolecular hydrogen bonds[17]. An obligatory condition is the presence in the substituent of one or several methylene groups, which separate the triple bonds and the functional groups of the substituents and whose purpose is to ensure the necessary flexibility in the rotation of the diacetylene groups during polymerisation with retention at the same time of the necessary interaction of the substituents.

Of the several hundred DA synthesised at the present time, only several tens proved capable of topochemical polymerisation. However, a polymer single crystal of large size and with a high degree of perfection cannot be obtained from all these monomers either. In certain cases the reaction does not lead to 100% conversion whatever the conditions. Furthermore, DA are known which are capable of existing in various crystalline modifications of which some are reactive, while others cannot be polymerised under any conditions[1,18-21]. Sometimes the monomer gives rise to up to 5 crystalline modifications on crystallisation[15,22]. All this shows that the geometrical packing of the molecules in the monomer single crystal, which specifies the distances between the reacting centres, and also the direction and the extent of the migrations of the atoms required for the reaction to occur are some of the decisive factors determining the reactivity.

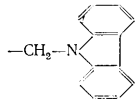
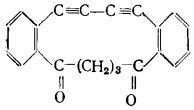
Table 1 presents the structural formulae and the abbreviations for the diacetylenes which polymerise quantitatively to give rise to polymers for which the greatest number of kinetic and physical investigations have been carried out.

III. THE MECHANISM AND KINETICS OF THE POLYMERISATION OF DIACETYLENES

The following features are characteristic of the polymerisation of the majority of DA:

(1) The polymerisation is initiated thermally, with the aid of ultraviolet light or X-rays, as a result of the application of hydrostatic pressure, and also under the influence of active gases, for example, halogens, nitrogen dioxide, ozone, etc.

Table 1. The structural formulae and abbreviations of the names of some of the most thoroughly investigated DA of the type R—C≡C—C≡C—R'.

R=R'	Abbreviation*
$-CH_2OH$	HD
$-CH_2OSO_2-C_6H_4-X$, X=CH_3	TS
X=OCH_3	MBS
X=F	PFBS
	DCHD
$-CH_2OCONHC_6H_5$	HDU
$-(CH_2)_4OCONHC_6H_5$	TCDU
$-(CH_2)_4OCONHC_2H_5$	ETCD
$-(CH_2)_nOCONHCH_2COOA$:	*n*ACMU
n=3, A=C_2H_5	3ECMU
n=3, A=C_4H_9	3BCMU
n=4, A=C_2H_5	4ESMU
n=4, A=C_4H_9	4BCMU
	BPG**

* To make it easier to become acquainted with the original literature, the abbreviations quoted for the DA are based on the most widely used English transcription.
** Cyclic monomer.

(2) On the basis of the kinetic curves, it is possible to distinguish autocatalytic (TS) and asymptotic (MBS) polymerisations§ (Fig.3). A fairly long induction period (up to 60 days at room temperature for TS) is observed in autocatalytic polymerisation during which an approximately 10% degree of conversion is attained, after which an autocatalytic stage is observed during which the latest polymerisation increases by a factor of several hundreds[24–27]; this stage is usually completed after the attainment of 100% conversion of the monomer.

(3) The range of variation of the activation energy in thermal polymerisation is fairly narrow, amounting to 80–105 kJ $mole^{-1}$.[25] For example, an activation energy of 94.3 kJ $mole^{-1}$ describes superbly the kinetics of the thermal polymerisation of TS in the temperature range 291–364 K, where the rates of polymerisation differ by a factor of 2400.[28]

§ The terms "autocatalytic" and "asymptotic" polymerisation are used for brevity in defining two different types of kinetics on the basis of the form of their kinetic curves. In fact the nature of the polymerisation is not autocatalytic[23].

(4) The polymerisation initiated by X-rays or ultraviolet light proceeds with an activation energy of approximately 10 kJ $mole^{-1}$.

(5) The activation energy for thermal polymerisation is constant over a wide range of conversions (up to 95%)[29].

(6) In the same range of degrees of conversion, the reaction is of first order with respect to the monomer.

(7) The pre-exponential factor in the expression for the first-order rate constant for thermal polymerisation in the autocatalytic stage is 10^{-8}–10^{-7} s^{-1}.[27,28]

(8) The capacity of the monomer crystal for polymerisation is determined by its previous history, in particular its crystallisation conditions[1,30] and purity[25].

(9) The polymerisation reaction is not initiated by radical initiators. Thus dicumenyl peroxide inhibits rather than initiates polymerisation[131].

(10) In many instances DA have two and more crystalline modifications differing sharply in their reactivity[15,22].

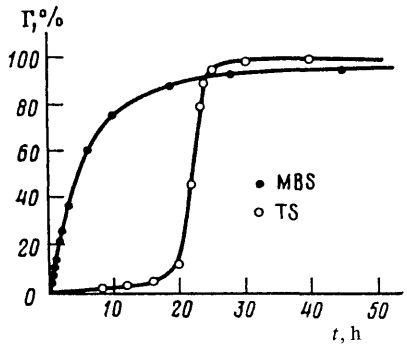


Figure 3. Kinetic curves for the polymerisation of TS and MBS at 333 K.[19] The degree of conversion of the monomer and the polymerisation time are plotted along the ordinate and abscissa axes respectively.

It is noteworthy that in the polymerisation of certain DA there may be deviations from the above rules. For example, the reaction sometimes ceases at a degree of conversion of 50–70%[16,32–34].

A kinetic mechanism of the solid-phase polymerisation of DA has been proposed by Baughman[35]. For autocatalytic polymerisation, the mechanism can be described qualitatively as follows. In the induction period stage of the polymerisation, oligomeric molecules with chain lengths corresponding to several tens of monomeric units are formed[28,36–38]. Since the transition from the monomer to the polymer crystal usually entails a decrease of the distance between the monomer units by 5–8%, the oligomeric molecules formed and the monomeric matrix are in a strained state: the bonds in the oligomeric molecules are extended relative to their equilibrium dimensions, while those in the monomer matrix are actually compressed. The elimination of these strains is accompanied by rapid polymerisation. At this instant the entire crystal decreases fairly rapidly in size in the direction of the growing chains (the *b* axis of the crystal lattice) and favourable energetic conditions are created for the occurrence of polymerisation.

The theory of topochemical polymerisation of DA was developed further in a study[39] where account was taken of a series of published comments and amendments. The observed

relation between the contraction along the *b* axis and the degree of conversion of the monomer (Fig.4) can serve as confirmation of this theory[40]. Analogous results have been obtained in dilatometric studies of the thermal TS polymerisation[41]. It has been established by dilatometric[40,41] and X-ray diffraction[38] methods that the lattice parameter along the *b* direction varies continuously with increasing degree of conversion. On the other hand, it has been found by the neutron scattering method[42] that this parameter changes abruptly. In contrast to γ-rays, a stream of neutrons does not initiate polymerisation and in this sense the neutron scattering method is more reliable; however, the experimental errors associated with this method are greater than in the case of the previous methods. At any rate, a correlation is always observed between the crystal lattice parameter along the *b* direction and the degree of conversion of the monomer. The interaction of the monomeric molecules during polymerisation is not accompanied by a change of the conditions along the *a* and *c* crystallographic directions. These results are fully consistent with the theory[35]. Generally speaking, the small change in the crystal lattice parameters on passing from the monomer to the polymer does not influence the feasibility of the polymerisation reaction and determines merely its kinetics and the quality of the final polymeric products.

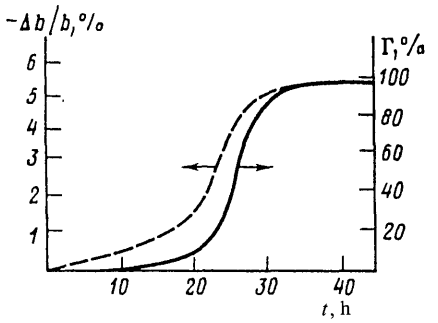


Figure 4. Kinetic polymerisation curve and the relative linear contraction of a TS single crystal along the *b* axis during thermal polymerisation at 323.2 K.[40]

The following postulates were made in the analysis of the kinetic polymerisation mechanism[35]: (1) the active centres are formed at a rate (calculated in terms of the concentration of the monomer which has not reacted) which is independent of the degree of conversion of the monomer; (2) the rate of deactivation of the active centres is independent of the degree of conversion of the monomer and is much greater than the rate of the competing chain initiation reaction; (3) the lifetime of the active centre propagating polymerisation is independent of the degree of conversion. In this mechanism the quantities which depend on the degree of conversion are the enthalpy components of the free energy for the initiation and chain propagation. This influence is due to the energetic strains in the reaction mixture matrix which is in the solid state.

Apart from the activation energy, the heat of polymerisation of various diacetylenes has also been determined. Over a wide temperature range, this quantity is −(120–150) kJ mole^{-1} for the majority of DA[24,43]. Furthermore, the heat of polymerisation has been calculated[25] with the aid of Dewar's "bond length–bond strength" relation and $\Delta H_p = -132$ kJ mole^{-1} for structure (B) of the polymer chain and $\Delta H_p = -123$ kJ mole^{-1} for structure (A) were obtained (Fig.1). The exothermic heat change is attributed to the addition of the monomer to the reactive end of the polymer chain.

It was later established in relation to 4BCMU¶ that the heat of polymerisation of the DA which polymerise predominantly only under the influence of illumination and γ-irradiation is much smaller than the usual values and amounts to approximately 100 kJ mole^{-1} (approximately 0.95 eV). Owing to the low heat of polymerisation, 4BCMU hardly undergoes thermal polymerisation. The low heat of polymerisation is attributed to the energetically unfavourable interaction of the side groups in the polymer compared with the monomer.

In discussing the mechanism of the thermal polymerisation, two structures are generally considered as the possible initiating species; the bicarbene structure $R\ddot{C}-C\equiv C-CR=RC-C\equiv C-C\ddot{R}$, first proposed by Wegner[22], and the biradical structure $R\dot{C}=C=C=CR-RC=C=C-\dot{C}R$. From the energetic standpoint, the formation of biradicals is more favourable than that of bicarbenes and there is a greater number of data showing that the biradical dimer is responsible for the initiation step[24,25,44,45]. Thus estimates of the energies of formation of bicarbenes and biradicals from the Dewar relations yielded 235 and 85 kJ mole^{-1} respectively[25]. However, EPR signals due to the bicarbene structure have been observed in the autocatalytic stage of thermal polymerisation[46–48]. It may be that a biradical is formed initially and then isomerises to a bicarbene[49].

The comparatively low ΔH_p constitutes indirect confirmation of the biradical mechanism of initiation[29]. Generally speaking, the initiation process and the structure of the final product are not related, since during polymerisation there are apparently transitions between the intermediate oligomeric molecules involving a decrease of multiplicity. The type of structure is then determined mainly by energetic factors, the electron energy, and the crystal strain energy. Virtually only the substituents determine the sequence of the bonds in the polymer chain.

Theoretical study of the unimolecular polymerisation initiation reaction using the Woodward–Hoffman rules[50] established that the formation of the monomeric bicarbene initiating species is photochemically allowed but thermally prohibited and, conversely, that the formation of a biradical is thermally allowed but photochemically prohibited. If there were no changes in multiplicity in the subsequent transformation, then thermal initiation would lead exclusively to form (B) of the polymers, while photochemical initiation would lead exclusively to form (A). In the study of initiation via the dimer, the conclusions concerning the formation of a biradical or a bicarbene being allowed in different types of initiation would apparently be the opposite to those established for the monomer.

Studies have been recently published whose authors note that the polymerisation model proposed[35] does not always make it possible to describe certain experimental results. For example, in the study of the thermal TS polymerisation under pressures[40,51], it was established that the reduction of the induction period of the reaction with increasing pressure is greater than predicted by the theory. Furthermore, in the investigation of the thermal polymerisation of the same monomer deuteriated in various positions[52], unusually large isotope effects were observed in the induction period stage of the polymerisation, which is difficult to explain in

¶ See H.Eckhardt, T.Prusik, and R.R.Chance, Macromolecules, 1983, **16**, 732.

terms of the theory[35]. A normal isotope effect is observed in the autocatalytic state.

An alternative model of the thermal polymerisation has been proposed[52], according to which excited states are constantly created in the monomer matrix. It has been suggested that the migration of the excitation energy in the lattice is a random process with considerable scattering[53]. In their diffusion pathway the excited states encounter randomly distributed but localised defects and are captured by them. If the lifetime of the excited state in such a trap is fairly long, then the state can serve as an initiator of chain polymerisation. Here there is a possibility of the following variants: (a) in the pure monomer matrix the concentration of defects is low and the rate of initiation is therefore also low; (b) for the average degree of conversion, the concentration of defects is large and many chain initiators are therefore formed, which leads to an increase of the overall rate of polymerisation. This approach explains the isotope effect and is consistent with the observed form of the kinetic polymerisation curve and with the earlier hypothesis that thermal polymerisation is initiated by the crystal defects[49,54]. The correctness of the choice of this type of polymerisation mechanism is confirmed by data concerning the influence of the previous history of the specimen, in particular its purity, on the duration of the induction period and the polymerisation rate constants[29]. Attempts have also been made to incorporate the influence of the anharmonicity of the bond vibrations and of the electron–phonon interaction in the explanation of the mechanism and kinetics of the polymerisation reaction[55].

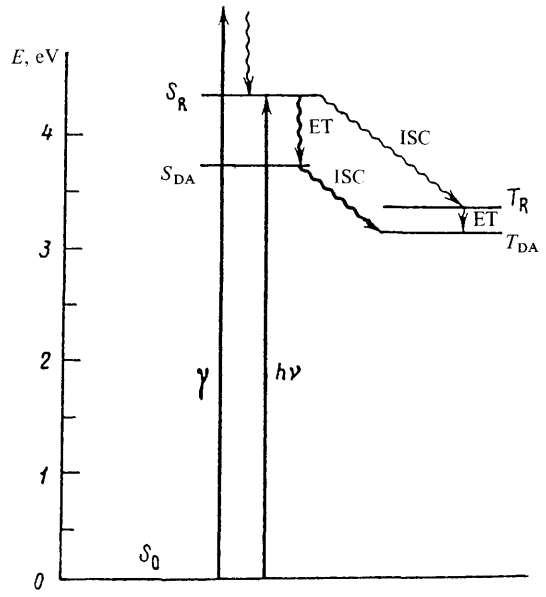


Figure 5. Diagram of the electronic levels of DA and the substituent R.[49] The possible pathways followed in the energy transfer are designated by thin wavy lines; the most probable pathway is shown by a bold wavy line.

Despite certain advances in the understanding of the mechanism and kinetics of thermal polymerisation, many problems remain unsolved. In particular it is not clear how energy is transferred to the reaction centre and is captured by it and the detailed mechanism of the initiation and the nature of the molecular excitation in thermal polymerisation are not understood. Indeed, the activation energy for thermal polymerisation $\Delta E_a \simeq 1.0$ eV,[49] while the energy of the lowest known triplet state in DA is approximately 3.1 eV[56]. The situation was actually made somewhat more complicated when it was established that certain DA are photopolymerised on sensitisation by phenazine[57,58] and by cyanine dyes[59,60]. Compared with DA, phenazine has a lower energy of the excited state[58] and therefore should inhibit rather than initiate the photopolymerisation of DA.

The influence of strain in the crystal on the polymerisation kinetics has not been ultimately elucidated either. In the study of the polymerisation of two monomers, MBS and TS, which have very similar molecular structures, it was established that MBS polymerises asymptotically[19,61], while a distinct autocatalytic stage is characteristic of the polymerisation of TS (Fig.3). Optical and Raman spectroscopic data have shown that during polymerisation the changes in the MBS and TS crystal lattices are the same[62], but the strain in the MBS crystal was greater than in the TS crystal[61,63]. Consequently the autocatalytic stage in the polymerisation of MBS should be more pronounced than for TS. Mixed crystals of the same monomers have been polymerised in different proportions[64]. With increase of the MBS content, the inductive period shortens. Since the crystal structures of these monomers are virtually identical, the differences between the polymerisation kinetics are hardly likely to be associated with the differences in the molecular packing and between the strains of these crystals. Analogous results have been obtained in the study of the polymerisation of mixed crystals of TS and diacetylenes with $R = R' = CH_2OSO_2C_6H_4X$, where X = Cl or Br[20,65]. This apparent contradiction can be obviated if it is supposed that the differences between the kinetics of the polymerisation of TS and MBS are associated with the longer lifetime of the active centre in MBS and hence with the larger pre-exponential factor[63]. Generally speaking, the two factors—the crystal strain and the lifetime of the active centre—are inter-related. Thus in the TS polymerisation it was observed by differential scanning calorimetry that the kinetics of the polymerisation reaction in the inductive period stage are virtually indistinguishable for single crystals of different qualities, whereas the rates of polymerisation in the autocatalytic stage can differ almost by an order of magnitude while the activation energy remains constant (93.4 ± 3.8 kJ mole^{-1}), which has been attributed to the difference between the pre-exponential factors due to the different strains in the single crystals[66].

The model of the polymerisation process involving the rotation of rigid diacetylene bonds in the plane of the polymer skeleton does not apparently fully correspond to reality and can describe the polymerisation process only in broad outline. It may be that the details of the topochemical polymerisation of diacetylenes can be understood when account is taken of the influence of low-energy phonons and also when one considers a reaction involving the rotation of non-rigid diacetylenic linkages with displacement of the carbon atoms from the plane of the skeleton†.

It is also incomprehensible why the kinetics obey the first-order law with respect to the monomer up to such high degrees of conversion.

A characteristic feature of the polymerisation induced by ultraviolet light and radiation is that it occurs regardless of whether an electronic state of the DA molecule is excited or whether the electronic excitation is initially localised at a

† See D.Bloor, Mol.Cryst.Liq.Cryst., 1983, **93**, 183.

substituent[22,67]. An electronic level scheme has been published[49] for substituted DA (Fig.5). The authors suggest the following scheme for the formation of active centres

$$S_0 + h\nu \rightarrow S_R \xrightarrow{ET} S_{DA} \xrightarrow{ISC} T_{DA} \rightarrow \text{polymer},$$

where S and T are the corresponding spin states of the DA and the substituent R, ET is the energy transfer, and ISC is intersystem crossing. All the energies of the electronic states of DA and the substituent, with the exception of the energy of the triplet state of DA, have been determined[49]. The only assumption made on the basis of the scheme is that T_{DA} lies below T_R. Later this hypothesis was confirmed and it was established that $T_{DA} = 3.1-3.2$ eV[56]. In this connection it is of interest to note that the polymerisation of the DCHD monomer is not initiated by ultraviolet light[68,69]. This can apparently be explained by the fact that the lowest excited energy state of the DCHD monomer is the triplet state of the carbazole group, i.e. the sequence in which the T_R and T_{DA} levels alternate changes (Fig.5) and the final stage of the energy degradation process is the triplet state of carbazole, which is incapable of initiating polymerisation. It can be assumed that the DA for which $T_R > 3.1$ eV will undergo photopolymerisation (provided, of course, that topological correspondence is observed).

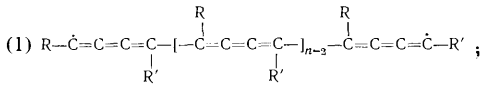
The kinetics of the polymerisation induced by ultraviolet light and radiation have been examined[49]. Both polymerisation stages are as a rule observed for these types of initiation: the induction period and the autocatalytic stage[49,70]. The study of the low-temperature photopolymerisation of DA led to a detailed determination of the initiation and chain propagation mechanisms, the chemical structure of the intermediate oligomeric chains, and also the multiplicity and the interconversions of various radical states of the growing ends of the oligomeric chains.

Biradicals[45,71] and symmetrical and asymmetric carbenes[45,46,71-76] have been detected by the EPR and optical absorption spectroscopic methods at 4.2 and 77 K in photoinitiated polymerisation. These states were identified as intermediate triplet states. For dimers and short oligomers, the interacting carbenes at the ends of the chains give rise to quintet[72,74,77,78] and singlet[74] states. Various types of intermediate species as well as the kinetics of their formation and destruction have been examined[67].

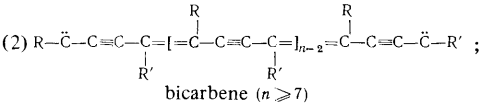
The polymerisation initiation process and the initial stage of the polymerisation have been thoroughly investigated at low temperatures, where the lifetimes of the excited initiating species and active polymerisation centres are sufficiently long to be determined experimentally. At low temperatures ($T < 200$ K) the initiation process is a two-quantum process[67,78], which follows from the experimentally observed quadratic dependence of the rate of formation of the active centres on the intensity of the irradiating light. The first absorbed quantum ($\lambda \lesssim 310$ nm) results in a transition of the monomer to an electronically excited state, which is converted into a monomeric biradical as a result of intersystem crossing[78]. The absorption of the second quantum results in the transition of the adjoining monomer molecule to a vibrationally excited state as a result of internal conversion. The combination of these molecules into a biradical dimer, capable of further chain propagation, actually constitutes the polymerisation initiation step. The subsequent photoreactions, consisting in the growth of the polymer chain by one monomer unit following the absorption of each quantum, is possible on irradiation with light at longer wavelengths, for example, 446 or 498 nm.[67]

At high temperatures ($T > 200$ K) there is a linear dependence of the rate of formation of dimers on the light intensity#, so that monomer molecules in vibrationally excited states are produced thermally.

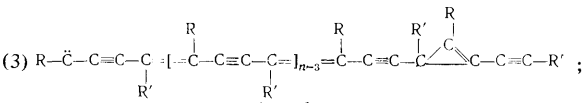
It has been possible to identify by the EPR method numerous intermediate triplet states of the oligomers in a low-temperature photoinitiated topochemical polymerisation[74]. It was found that there are only four types of products with different chain lengths§



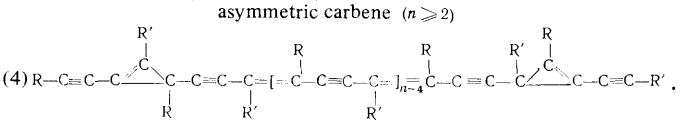
(1) biradical ($2 \leqslant n \leqslant 6$)



(2) bicarbene ($n \geqslant 7$)



(3) asymmetric carbene ($n \geqslant 2$)



(4) stable oligomer ($n \geqslant 3$)

Among all the details of the structures represented, only the existence of the pseudocyclopropene ring is hypothetical and is based on the assumption of the intramolecular deactivation of the active centres. It has been postulated that the pseudocyclopropene structures are stabilised by the molecular field of the crystal.

Analogous studies designed to discover the intermediate photopolymerisation products and to determine their nature have been carried out in connection with the photopolymerisation of TS at high temperatures[79]. A specially devised method was used to record the optical absorption spectra of short-lived (< 50 μs) intermediate species. The essential feature of the method was that it involved the recording of differential absorption spectra representing the difference between the absorption spectra after irradiation with a laser pulse ($\tau = 15$ ns, $\lambda = 308$ nm) and before irradiation. Several similar spectra have been recorded over a period of approximately 10^{-5} s. This method makes it possible, firstly, to isolate the spectra of the newly formed photoproducts and their measurement is not interfered with by traces of the polymer present in the specimen and, secondly, one can detect extremely short-lived species and investigate the kinetics of their formation, their interconversions, and destruction.

At least five intermediate species were detected, of which only one, having the maximum at the shortest wavelength in the absorption spectra, is a direct consequence of irradiation with light and was identified as a dimer. The remaining four products arise from the consecutive addition of monomer molecules, which takes place as thermal processes. The activation energy for the addition of the monomer is 0.25–0.30 eV and the pre-exponential factor is approximately 10^{11} s^{-1}. At low temperatures the quantum yield in

See H.Gross, W.Neumann, and H.Sixl, Chem.Phys. Letters, 1983, **95**, 584.

§ H.Gross and H.Sixl, Chem.Phys.Letters, 1982, **91**, 262.

the formation of dimers $\Phi \cong 10^{-2}$, diminishing to 10^{-3}–10^{-4} s with increase of temperature. The quantum yield Φ is highest for the defect-free monomer single crystal, but there are no channels for the transfer of energy to defects and the growing polymer chain.

The overall quantum yield (the number of polymerised monomeric units per absorbed light quantum) varies within wide limits: from 0.06 for TS (Bhattacharjee and Patel[80]) to 50 (Bhattacharjee and Patel[80]) and 90 (Shand and Chance[81]) for 4BCMU. Here one can trace a kind of compensation effect: the DA which have a high ($\gg 1$) polymerisation quantum yield do not undergo effective thermal polymerisation, while the DA which do undergo effective thermal polymerisation have a low ($\ll 1$) photopolymerisation quantum yield. Chemical actinometry[80] and photoacoustic spectroscopy[81,82] were used to determine the quantum yield. It was found that the rate of the photoinitiated polymerisation of DA greatly diminishes with increasing degree of conversion[83], which can be explained by energy transfer from the excited state of the monomer to the polymer chain. Such transfer is an important rate-limiting factor in photopolymerisation and must be taken into account in the determination of the quantum yield.

The kinetic polymerisation chain length depends on the stress applied to the monomer lattice[53]. The chain character of the photopolymerisation process has been demonstrated by photoacoustic spectroscopy[82]. Estimation of the lifetimes of the excited states yielded values differing by several orders of magnitude, from 10^{-3} s in the studies of Wegner and co-workers[52,53] to approximately 10^{-6} s in the study of Chance and Shand[82].

The photoinitiated polymerisation has been studied with irradiation of TS crystals by light through a dense grid under normal conditions[84] and with application of hydrostatic pressure[85]. Subsequently the reaction front profile in the shadow zone was investigated by scanning electron microscopy. The spatially isotropic growth of the polymer chains in the shadow zone and not only along the directions of the chain indicates the initiation in the primary step. Indeed, when one monomer molecule adds on, the energy liberated is 1.6 eV,[24] which exceeds the activation energy for the reaction ($\Delta E_a \cong 1.0$ eV). The excess energy liberated spreads isotropically from the reaction zone and gives rise to the vibrational excitation of the adjoining DA molecule, initiating thereby secondary polymerisation.

The photosensitised polymerisation of diynoic acid mixed with phenazine[57,58] and the autosensitised photopolymerisation of multilayers[86] can be explained analogously. The application of an electric field does not alter the rate of reaction or the profile of the reaction front; consequently the hypothesis[86] of the secondary initiation with the aid of the free carriers generated on deactivation of the electronically excited state is unfounded. A number of features of the photopolymerisation sensitised by cyanine dyes[59], in particular the independence of the maximum degree of conversion and the dye concentration and the high (approximately 90 Å) sensitisation radius[60] can be explained within the framework of the model postulating thermal initiation by the excess thermal energy liberated in the course of the u.v.-initiated polymerisation.

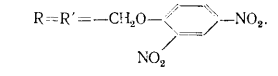
Similar results were obtained on sensitisation of the photopolymerisation by acridine and anthraquinone dyes¶, which are electron donors, in contrast to cyanine dyes. The authors of the above study nevertheless hold the view that charge transfer plays a decisive role in the photoinitiated polymerisation sensitised by electron-donating and electron-accepting dyes. The quantum yield of the photopolymerisation sensitised by cyanine dyes is in the range $0.7 \times 10^{-3} < \Phi < 17 \times 10^{-3}$: the corresponding values for the acridine and anthraquinone dyes are 2×10^{-3} and 7×10^{-3} respectively.

The radiation-initiated polymerisation of the various DA is characterised by a greater difference in the number of polymerised monomeric units per 100 eV of the irradiation energy [$G(-m)$]. Thus $G(-m) \cong 2 \times 10^5$ for 4BMCU[87] and $G(-m) = 66$ for TS[37,87]. When the substituents are altered, the sensitivity of the DA to ionising radiation on polymerisation can change by 6–7 orders of magnitude[87]. It has been suggested that the initiating species in the γ-initiated polymerisation is a biradical dimer[44,71]. The difference between the types of initiating species in photopolymerisation and γ-polymerisation is apparently associated with different selection rules for electronic transitions in various types of initiation.

In the study of polymerisation under the conditions of hydrostatic pressure, it was established[40,51] that, as in polymerisation under normal conditions, the reaction is first order with respect to the monomer up to 90% conversion and that pressure does not alter the activation energy for initiation and chain propagation. However, with increase of pressure, there is a decrease in the induction period, which disappears at $p > 3$ kbar; the polymerisation rate constant increases exponentially with increase of pressure. The increased rate constant for the reaction is attributed mainly to the component of the hydrostatic pressure acting at right angles to the direction of the growing chains and inducing the mutual approach of the hydrocarbon atoms of neighbouring monomeric units, which promotes the reaction. The decrease and even the disappearance of the induction period with increase of pressure is apparently associated with the fact that, under these conditions, the crystal lattice parameters in the monomeric and polymeric phases are equalised.

In the initial stage of polymerisation fairly long oligomeric chains are formed rapidly for all types of initiation[88]. The degree of polymerisation changes from $n \cong 20$ at the beginning of the induction period to $n \cong 40$ at the end of this period and reaches $n \cong 140$ in the autocatalytic stage[28]. At the instant of the completion of the polymerisation, n increases still further.

The molecular weight distribution in the initial stage of the polymerisation has been investigated† by an independent method—with the aid of X-ray diffraction for DA and TS with substituents:



The latter monomer polymerises fairly slowly under the influence of γ-rays and the molecular weight distribution curves and the average degrees of polymerisation could be determined for this monomer during the polymerisation reaction. Their values, which are close to those determined previously, are following values for different degrees of conversion Γ: $n = 22$ ($\Gamma = 0.65\%$), $n = 38$ ($\Gamma = 4.5\%$), and $n = 47$ ($\Gamma = 16\%$). Analogous results were obtained for the polymerisation of TS.

The molecular weight distributions for soluble PDA [poly-(3)4BCMU] have been determined by gel permeation chromatography[89,90] and $M_n = 49 \times 10^5$ g mol^{-1} (poly-3BCMU, $n \cong$

¶ See C.Bubeck, K.Weiss, and B.Tieke, Thin Solid Films, 1983, **99**, 103.

† See P.A.Albony, J.N.Patillon, and J.P.Pouget, Mol. Cryst.Liq.Cryst., 1983, **93**, 239.

10^3)[90] and $M_n = 1.2 \times 10^6$ g mol^{-1} (poly-4BCMU, $n \cong 2.4 \times 10^3$)[89] were obtained; the polydispersity index is $M_w/M_n \cong 5$.

Later more detailed studies were made[91] of the molecular weight distribution (MWD) for poly-3BCMU in γ-initiated polymerisation with various irradiation doses in the range from 0.09 to 45 Mrad and fairly high molecular weights and narrow MWD were obtained for small doses ($M_n = 1.33 \times 10^6$ g mol^{-1}, $M_w = 3.9 \times 10^6$ g mol^{-1}, $M_w/M_n = 2.93$, dose = 0.09 Mrad). The values of M_n and M_w diminish significantly with increase dose of radiation and the polydispersity index increases very strongly; for example, $M_n = 1.79 \times 10^5$ g mol^{-1}, $M_w = 2.31 \times 10^6$ g mol^{-1}, and $M_w/M_n = 12.8$ have been obtained for a dose of 15 Mrad. As the irradiation dose is increased from 0.09 to 45 Mrad, the degree of conversion of the monomer rises from 21% to 49%. The decrease of the molecular weight of the polymer is attributed to degradation during irradiation. High molecular weights have been obtained for PDA with R = R' = $(CH_2)_5OC(O)X$ in a study by Plachetta and Schulz[92]: $M_n = 2.4 \times 10^5$, 3.4×10^5, and 3.2×10^5 g mol^{-1} and $M_w/M_n = 3.33$, 3.94, 3.75 for X = $CH(CH_3)_2$, $CH_2C_6H_5$, and CH_2-α-naphthyl respectively.

Analogous studies have been carried out for poly-TS at conversions from 0 to 12%, at which the polymer is still soluble[37]. In this range of degrees of conversion the MWD is fairly broad and does not change with the degree of conversion and $n \cong 20$. It may be that this low value of n is due to the degradation of the polymer in the strong solvent (dimethylformamide, chloroform) used in the determination of the MWD[93], since $\bar{M}_n$ determined by other methods is much greater[24,38].

IV. THE ELECTRONIC STRUCTURE OF POLYDIACETYLENES

Polydiacetylenes constitute a convenient and unique object for the theoretical description and investigation of the electronic structures of polyconjugated systems. There are exhaustive data on the structures, bond lengths, and valence angles of certain PDA. There are also extensive experimental data for the optical properties of these polymers[4,5]. The energies and polarisations of the electronic transitions have been determined on the basis of these results and the vibrational energies of the excitation of various bonds have been found from infrared and Raman spectroscopic data[6]. The polymers considered are of interest also because they constitute in essence a model one-dimensional system of virtually infinite length made up of rigorously repeating monomeric units without defects in the structure and conformation of the chains. This simplicity of the structure is, however, only apparent. Calculation of the electronic structure and ultimately the understanding of the physical properties are complicated by the interaction of the side groups of a single chain and also by the intermolecular interaction between chains.

The studies which have been made on the electronic structure of PDA were devoted mainly to the elucidation of the nature of the long-wavelength optical absorption with an energy of approximately 2 eV, the influence of the substituents and external conditions on the electronic structure of PDA, and also certain electrophysical properties.

In the study of the electronic structure of PDA many unsolved problems are common to all types of conjugated systems, for example, the question of the nature of the forbidden energy gap in the spectrum for one-electron excitations. So far there is no unanimous view concerning the origin of this gap even for polyene systems. The extreme views are that the gap can be attributed either to the alternation of the bond lengths (the Peierls instability of the one-dimensional metal relative to the doubling of the crystal lattice period) or that its nature is of the correlation type (the Mott–Hubbard electronic phase transition due to the electron interaction). For conjugated systems, this problem has been investigated in detail[94] and the hypothesis that the nature of the energy gap is of the correlation type appears to be supported by the soundest arguments.

The question of the nature of the energy gap in PDA is masked by the fact that the alternation of bond lengths is a permanent property of these systems, which can be readily adopted as the cause of the appearance of the energy gap. In describing the electronic structure of PDA, one must bear in mind all the theoretical data which have accumulated on conjugated systems and studies must be made taking into account the electron interaction. The question of the nature of the gap in PDA was specially studied[95] with the aid of a modified Hubbard Hamiltonian; it has been shown that the contribution of the Coulombic correlations to the energy gap is approximately 1.9 eV and that the exciton band is split off from the conductivity band only when account is taken of the electron interaction at the neighbouring atoms.

Table 2. Results of the calculations of the width of the forbidden gap ΔE for PDA.

Method of calculation	Free electron[a]	Hückel	Extended Hückel[b]	X_α^c	PPP + CI[d]	LCAO-MO SCF[e]	LCAO-MO + CI[f]	CNDO/S + CI	STO-3G basis	7s/3p basis	Effective Hamiltonian	ΔE_{exp}, eV
ΔE, eV	2.0	1.36	1.0; 1.22	2.21	1.31–1.42[g]	0.25–0.51	2.0–4.0[g]	4.09–4.38	4–11	—	2.1	1.9–2.6[h]
R=R'	—	—	C≡C–H; H	—	H	NH_2; CH_2OH	—	H	H; F	H	H	i
Refs.	[96]	[97]	[98, 99]	[100, 101]	[102]	[103]	[104, 105]	[106]	[107–109]	[110]	[111, 112]	

Remarks: [a] A modified method of free electrons with sinusoidal modulation of the potential was used; [b] the numerical values quoted in accordance with Parry's data[98]; [c] the calculation was performed for the model compound 1,5,9-tridehydro(12)annulene; [d] Ono's parametrisation; [e] the gap width for seven substituents was calculated by Parry[103]; here the minimum and maximum values are quoted; [f] Yarkony[104] used the experimental geometry corresponding to poly-TS and poly-TCDU; [g] the scatter of the values is associated with the different geometries chosen for the molecule for which the calculations were made; [h] the gap widths determined from the positions of the optical absorption maxima are quoted; the width of the forbidden gap is greater by several tens of electron-volts; [i] the literature data are quoted in Section V of this review.

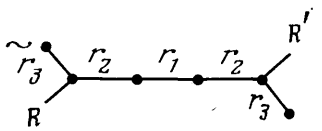
The range of suitable methods for the study of the electronic structure of PDA is fairly broad: from the simple free electron in a potential box and Hückel methods to non-empirical calculations. Attention has been concentrated in the calculations on the correct description of the energy of the longest-wavelength optical transition. A satisfactory description of this quantity is usually regarded as one of the principal criteria of the applicability of a particular computational method. The results of the calculations of the width of the forbidden gap are presented in Table 2. Evidently

satisfactory optical excitation energies are obtained, as was to be expected, only in calculations which include the configurational interaction, which takes into account partly the electron interaction. Much attention has also been devoted to questions of the relative stabilities of structures (A) and (B) and a correct description of the behaviour of the energy gap in the excitation spectrum in the transition (A) → (B). The ground state of the PDA chain is structure (A). A non-empirical calculation[110] with the optimisation of bond lengths and angles in terms of the 7s/3p basis set showed that structure (A) is more stable by approximately 50 kJ mol^{-1} per C_4H_2 unit than structure (B). In order to understand the nature of this transition, it is necessary to go beyond the limits of the Hartree–Fock approximation.

As an illustration of the relative nature of the concepts concerning structures (A) and (B) of the PDA chain which have been introduced, Table 3 presents the experimental and calculated bond lengths in real and model PDA. It is evident that, although poly-PTS, poly-DCHD, and poly-HDU have been arbitrarily assigned to the (A) type while poly-TCDU and poly-BPG have been assigned to the (B) type, nevertheless the bond lengths in polymers of both types are fairly remote from the theoretical values calculated for the model compounds.

Theoretical studies have led to certain general conclusions. The long-wavelength optical absorption has an exciton character. The difficulties associated with the correct description of the behaviour of the energy gap in the (A) → (B) transition indicate a number of factors which have not been taken into account, such as the influence of the intramolecular and intermolecular forces in the interaction between chains and also the influence of substituents. If the overall energy of the crystal is divided arbitrarily into two components—the electronic energy and the crystal field energy, then the above effects can in fact be attributed to the crystal field energy.

Table 3. The carbon–carbon bond lengths in the main chains of various PDA determined by X-ray diffraction (in accordance with Karpfen's data[110]) and calculated by the *ab initio* method in terms of the STO-3G basis set for the "ideal" structures (A) and (B)[108]



Polymer	r_1, Å	r_2, Å	r_3, Å
Poly-PTS	1.19	1.43	1.36
Poly-DCHD	1.21	1.44	1.33
Poly-HDU	1.21	1.41	1.36
Poly-TCDU	1.24	1.37	1.44
Poly-BPG	1.29	1.38	1.42
Structure (A)	1.20	1.45	1.34
Structure (B)	1.26	1.35	1.48

At the present time there are no theoretical methods whereby one could calculate simultaneously and with self-consistency both energy components. It is therefore necessary to justify model concepts which makes it possible to take into account in the first place the intermolecular interactions and their influence on the electronic structure of PDA. Numerous experimental results have shown that the forces governing these interactions are fairly large.

V. THE OPTICAL PROPERTIES OF POLYDIACETYLENES

The intense optical absorption of photons with an energy of approximately 2 eV ($\lambda_{max} \cong 620$ nm) is due to the presence of the conjugation system in PDA and in this sense the latter resemble polyenes[96]. However, in contrast to the optical spectra of the known polymers with conjugated bonds, having a broad structureless maximum and a long-wavelength absorption "tail",[113] the PDA spectra have characteristic features whose broad outline can be seen from Fig. 6.[114] The anisotropy of the crystal structure of PDA is responsible for the anisotropy of virtually all the physical properties including optical properties. The optical absorption therefore depends on the polarisation of light relative to the crystallographic axes. For light polarised parallel to the plane of the conjugation chain, a sharp absorption edge is observed in the region of approximately 2 eV, where a fairly narrow maximum is observed in reflection spectra. The smallest energy of the optical transition in solid PDA (approximately 1.89 eV) has been obtained for poly-DCHD.[115] The degree of dichroism of PDA single crystals is fairly large; thus in the case of poly-TS, for light polarised approximately parallel to each of the three principal crystallographic axes, the absorption coefficients at $h\nu \cong 2$ eV are respectively 9×10^5, 2×10^3, and 5 cm^{-1}.[5] Analogous results have been obtained for other PDA[89,115,118]. For partly polymerised specimens, the edge of the absorption band and the reflection maximum are more diffuse[114], but their positions are related to the kinetic polymerisation curve: at the instant when the autocatalytic stage begins, there is also a sharp bathochromic shift of the absorption edge and reflection maximum frequencies[119].

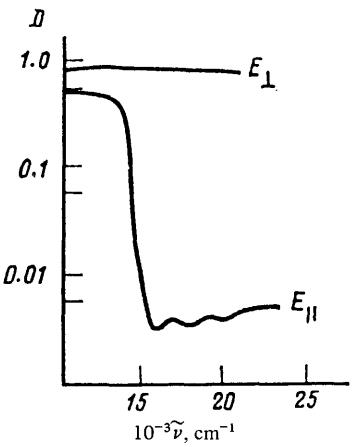


Figure 6. Optical transmission spectrum of a single crystal of poly-TS for light polarised parallel ($E_\parallel$) and at right angles ($E_\perp$) to the *b* axis.[114]

The initial DA are usually colourless or only slightly coloured. Changes in the colour of the partially polymerised DA are already observed for a monomer conversion of approximately 0.01%, since the molar absorption coefficient of

PDA is very high ($\varepsilon \geq 1.7 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[120,121] As polymerisation proceeds, the colour deepens and at the end of the polymerisation reaction the PDA usually has a metallic lustre with various colour tints. In terms of colour and other optical characteristics, PDA can be divided into two categories. The first includes PDA coloured reddish-gold and the second PDA coloured green and blue. PDA with sulphonate substituents (poly-TS, poly-MBS) belong to the first category and those with urethane substituents (poly-TCDU, poly-ETCD, etc.) belong to the second[122]. The number of methylene groups in the diacetylene $X-(CH_2)_n-C\equiv C-C\equiv C-(CH_2)_n-X$, separating the functional groups X (urethane, sulphonate etc.) and the triple bond, is apparently more important for the colour of PDA than the type of substituent[8]. Thus the majority of partly polymerised DA with $n = 1$ and 2 are red and those with $n = 3$ and 4 are blue.

In order to extend the range of the colour changes, DA with the chromophoric azobenzene groups $-C_6H_4N{=}NC_6H_5$ in the side chains have been synthesised[43]. At a low degree of conversion, the colour of the DA is determined by the chromophores. The partly polymerised DA has a colour which is determined both by the chromophores and by the absorption due to the conjugation chain. At a degree of conversion $\gtrsim 10\%$, the colour is determined mainly by the absorption due to the conjugation chain in the macromolecule formed.

Various optical methods, mainly transmission or reflection spectroscopy, have been used to investigate PDA. For a fully polymerised specimen, the depth of penetration of light in the most interesting spectral region is approximately only 100 Å,[16] which imposes definite limitations on the applicability of the technique of transmission spectroscopy. With the aid of this method, the greatest reliability of the results is achieved in the study of specimens with low (approximately 1%) degrees of conversion. Parameters such as the absorption band shape, the absorption coefficient, and others are then measured directly.

On the other hand, the possibilities of reflection spectroscopy are manifested most effectively in the study of specimens with a high degree of conversion. The determination of the spectroscopic parameters involves in this instance the application of the Kramers–Kronig dispersion relation between the real and imaginary components of the complex dielectric constant. The procedure whereby the absorption spectrum is deduced from the reflection spectrum with the aid of the dispersion relation is not unambiguous, since there is an uncertainty associated with the necessity for extrapolations. However, the results obtained with the aid of transmission and reflection spectroscopy agree[116].

The long-wavelength optical absorption was initially attributed to the direct interband electron transition from the valence to the conductivity band, which was seemingly confirmed by the analysis of the optical absorption line forms of certain PDA.[114,123–126] This analysis indicated the existence of a one-dimensional Van Hove singularity, which arises in a vertical interband transition when there is a plateau on the dispersion curve relating the energy to the wave vector.

On the other hand, there exists much evidence supporting the view that the long-wavelength edge of the optical absorption band is associated with exciton absorption. One of the most important indirect arguments in support of this view is the absence of photoconductivity at the optical absorption edge of PDA[127,128] and the hypsochromic shift of the maximum in the photoconductivity spectra relative to the maximum in the absorption spectrum. The magnitude of this shift is 3000 cm^{-1} for poly-TS[127] and is anomalously large (approximately 15000 cm^{-1}) for poly-CDU.[117] Consequently the long-wavelength optical absorption gives rise to an excited state. This excited state is most probably an exciton. The evidence in support of the exciton nature of the absorption is also provided by the lateral phonon bands in the optical absorption spectra and by the resonance Raman scattering[114]. Apart from indirect data, there exists also direct experimental evidence that the long-wavelength optical absorption in PDA has an exciton character. Surface exciton states have been observed for poly-TS[129,130] and the method of electric field-modulated reflection spectroscopy yielded analogous results: the width of the forbidden gap is $\Delta E = 2.44$ eV for poly-TS[131,132] and $\Delta E = 2.335$ eV for poly-DCHD[133]. The reflection spectra of both polymers showed a signal due to the exciton absorption for an energy smaller by 0.48 eV than the width of the forbidden gap[134]. Identical results have been obtained in the study of poly-TS in polarised thermo-reflection#. In this method the temperature of the specimen is modulated (frequency ~ 1 Hz, amplitude ~ 1 K) and derivatives of the absorption spectrum in polarised light are recorded. This method is extremely sensitive, particularly in relation to the temperature-dependent regions of the TS spectrum. The following data have been obtained with its aid: the exciton absorption begins with an energy of 2.00 eV and the width of the forbidden gap is 2.44 eV. The results of the analysis of the optical absorption line form near its absorption edge have also been revised recently. It has been found that the asymmetric Lorentz form, corresponding to the exciton model, provides the best description of the experimental line[5,116,135]. A similar ambiguity in the treatment of the line form also arose in connection with the narrow energy range in which linearisation was carried out and with the errors associated with this factor.

An interesting feature of the TS monomer and of its partly and fully polymerised specimens is that at low temperatures all the lines observed in the optical absorption and reflection spectra[123,126,136–138], the piezomodulated absorption spectra[136], the Raman spectra[138], and the EPR spectra[76] are divided into doublets. The splitting is observed down to the very lowest degrees of conversion (1%)[138] and even for the pure monomer[38]. The splitting in the optical spectra at 300 K is almost zero, but increases monotonically with decrease of temperature, amounting to 30 meV at the helium temperatures. Line splittings are not observed in the optical spectra of other PDA[115,117,124,125]. In order to explain this phenomenon, it is necessary to answer two fundamental questions: firstly what is the nature of the splitting of the bands and secondly why is it observed only for TS and its polymer.

The first attempts to account for the band splitting were made on the basis of X-ray diffraction data. It was established that the size of the unit cells of TS and its polymer is doubled in the low-temperature phase along the *a* crystallographic direction[135,140,141]; the number of monomeric units in the unit cell of the crystal is also doubled, which can be explained by the changes in the distances between the monomeric units in pairs owing to the reorientation of the substituents[141,142]. As a result, each of two types of molecules has a different environment and in such a situation it is logical to expect the splitting of all the observed lines to give doublets.

It has been suggested that the observed transition is a second-order phase transition[142,144]. In the study of this phase transition by spectroscopic methods[142,143], the critical

See S.Stizza, I.Davoli, V.Prantera, A.Bianconi, J.Glinski, and J.Kalinowski, J.Phys.C., Solid State Phys., 1983, **16**, 2165.

parameters were determined and an attempt was made to determine the order parameters. Comparison with the available exact results based on the theory of critical phenomena established that the two-dimensional phase transition apparently takes place at low temperatures, acquiring a three-dimensional character in the vicinity of the critical temperature. The broad temperature range of the transition indicates the important role of fluctuations. Regions with an altered orientation of the groups arise at random throughout the bulk of the specimen and are of the fluctuation type, so that reorientation is hardly likely to occur simultaneously. The character of the temperature dependence of the line splitting of the spectra (the logarithm of the splitting energy varies linearly with the lattice parameter along the *c* crystallographic direction) shows that the splitting is two- or three-dimensional[145].

In order to identify the nature of the band splitting in the spectrum of poly-TS, the PFBS monomer, isomorphous with TS, in which the intermolecular interaction is stronger owing to the presence of the fluorine atom which also has a van der Waals radius close to that of the methyl group, was synthesised[146]. However, it was found that, although the optical and Raman spectra of poly-TS and poly-PFBS are virtually identical at 300 K, there is no band splitting in the spectrum of poly-PFBS even at low temperatures[139]. Clearly the band splitting is not associated with the intermolecular interaction of the polymer chains[147,148] and is due to the existence of two types of polymer chains having different environments.

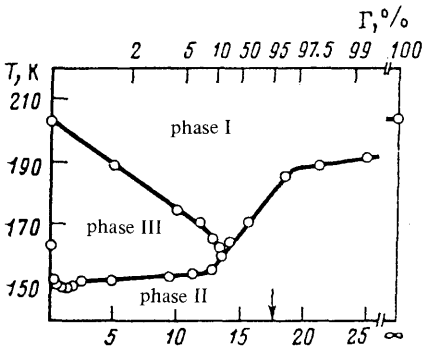


Figure 7, Phase diagram of partly polymerised TS.[154] The arrow denotes the instant of the maximum rate of polymerisation (at 60 °C) during the autocatalytic stage; phase I—single crystal with two monomeric units ($z = 2$) in the unit cell; phase II—$z = 4$; phase III—incommensurable phase.

The situation became more complex and more difficult to explain when yet another, third stable phase, corresponding to an incommensurable modulated structure, was observed in the spectrum of TS for a degree of conversion < 50%[150-152] (Fig.7). The temperature range corresponding to the existence of this phase is a maximum for a low degree of conversion (~ 1%) and is between 163 and 206 K, becoming gradually narrower with increase of the degree of conversion and disappearing in the autocatalytic stage. According to X-ray diffraction data, the incommensurable phase is modulated with a wave vector $\mathbf{q} = \frac{1}{2}\mathbf{a}^* + (T)\mathbf{b}^*$,[153,154] where the lattice period along the *b* direction depends on temperature. The intensities of the corresponding satellite lines in X-ray diffraction vary in accordance with the law $(T_c - T)^{2\beta}$, where $\beta = 0.43$ and $T_c = 199.2$ K. The critical exponent for the specific heat is approximately 0.7, which is too large for any simple model[150].

Two features of the incommensurable phase were observed by low-frequency polarised Raman scattering: (1) at temperatures approximately 15 K below the critical temperature, the existence of a soft mode (amplitone) was observed, the mode becoming softer as T_c is approached from the low-temperature side; (2) the line observed at 13 cm^{-1} is characteristic only of the incommensurable phase[153]. The first feature shows that for $T < T_c$, there is a mutual displacement of the monomeric units or parts from the latter relative to one another. When static shifts of this kind become commensurable with the average phonon vibration amplitude, the multiphonon scattering process is transformed into first-order Raman scattering, which is the reason for the appearance of the line at 13 cm^{-1}.[153]

In the study of the pyroelectric effect for TS along the *b* direction over a wide range of degrees of conversion, it was found that, when the temperature is altered, the pyroelectric coefficient has maximum values near the phase transition temperatures[155]. The phase transition temperatures agree well with those obtained previously[154]. The existence of the pyroelectric effect shows that the crystal loses its centre of symmetry and that the extent to which central symmetry is lost is a maximum near the critical temperatures, possibly owing to the occurrence of macroscopic fluctuations.

Anomalies have also been observed in the rate of propagation of sound§, showing that the phase transitions in the monomeric TS single crystal occur at 159 and 192 K and those in the polymer occur at 196 K.

Sharp phase transitions were detected with the aid of the methods enumerated above as the temperature was varied; however, the optical splitting varies smoothly with temperature. The causes of such behaviour are still obscure. Nor is the detailed nature of the formation of the incommensurable structure itself in TS and its partly polymerised crystal clear. It may be that the identity of the modulation wavelength of the incommensurable structure (b^*/δ) with the chain length of the polymer during the inductive period is not fortuitous[28].

(a) Thermochromism and Solvatochromism

The phenomenon of thermochromism, i.e. the change in colour with temperature, is normally confined to the bisurethane polymeric derivatives of diacetylene; poly-TCDU[117,156,157], poly-ETCD[158,159], and others. For example, the crystal of poly-ETCD is green in reflected light at a temperature below that of the colour transition, while above the transition temperature it acquires reversibly a red colour[158]. Changes in the reflection spectrum appear at 115 °C and cease at 130 °C. Subsequently on heating to 180 °C, no changes take place in the spectra. The shift of the maximum in the reflection spectra of poly-ETCD is hypsochromic and amounts to approximately 2750 cm^{-1}. With decrease of temperature the reverse colour change occurs at a temperature (approximately 70 °C) differing greatly from that of the forward transition. Such marked hysteresis is typical for thermochromism in PDA and is evidence for the occurrence of a first-order phase transition. The observed thermochromic transition is multiply reversible. Thermochromism is observed not only for single crystals[33,160] but also for amorphous film and solutions[89,161-163].

§ See W.Rehwald, A.Vonlanthen, and W.Meyer, Phys. Stat.Solidi, 1983, **B.A75**, 219.

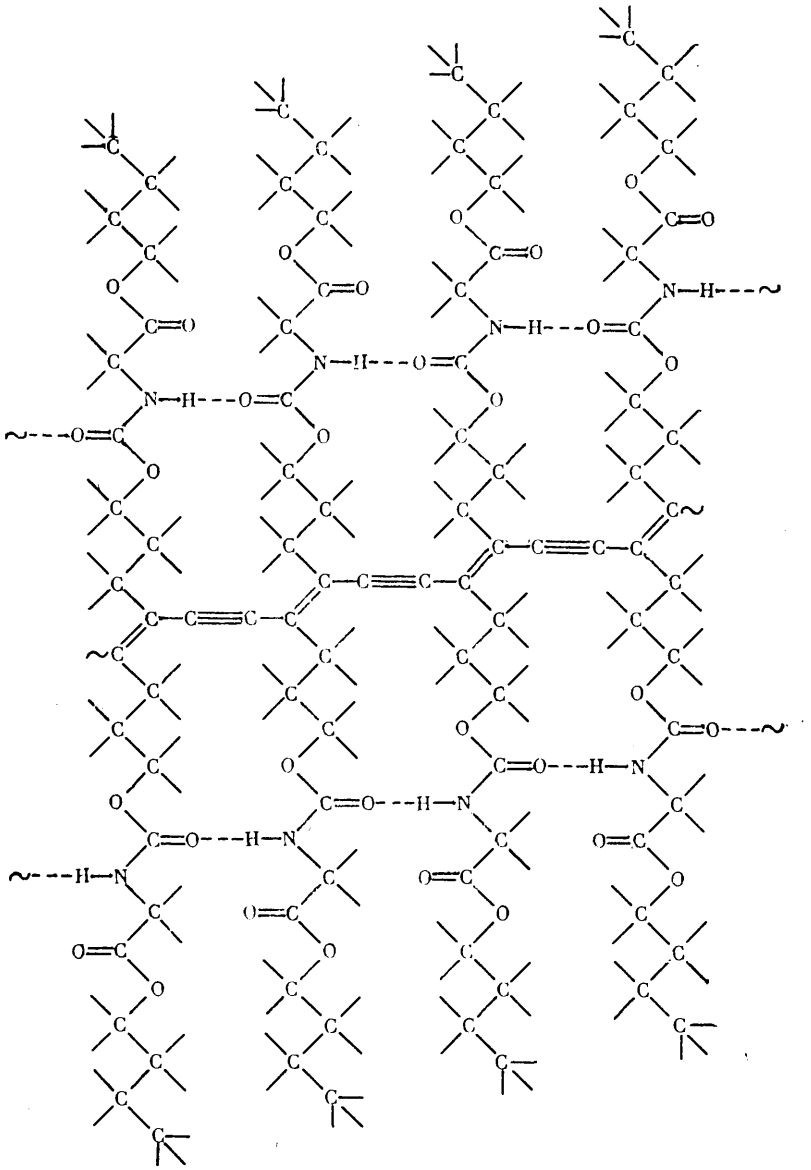


Figure 8. A fragment of the chain of poly-3BCMU in the planar conformation; the intramolecular hydrogen bonds are shown dashed[121].

For partially polymerised *n*ACMU (n = 3,4; A = E,B) and a degree of conversion of approximately 5%, the changes in colour from dark-blue to red with increase of temperature to the melting point take place smoothly. For fully polymerised specimens, the colour changes take place abruptly, over a range of approximately 5 K, and only two colour transitions are observed (Table 4). Two endothermic peaks at the temperatures corresponding to the colour change have also been observed by differential scanning calorimetry[164]. The first endothermic peak is associated with the fusion of the polymer, which remains oriented due to hydrogen bonding. The second endothermic peak is associated with the rupture of the hydrogen bonds and the complete fusion of PDA[165]. Fig. 8 presents as an example a fragment of the chain of poly-3BCMU with intramolecular hydrogen bonds. The shift of the maxima in the reflection spectra of substituted bisurethane PDA in thermochromic transitions is approximately 3000 cm^{-1} and with increase of temperature the position of the maximum changes from 15500 to 18500 cm^{-1}.[89,117,158] Sometimes the shift of the maximum can approach 5000 cm^{-1}.[121]

The temperature range in which thermochromic transitions are observed for PDA is fairly broad and is not limited to positive temperatures. Changes in colour are observed for a series of PDA down to approximately −200 °C.[8] For example, the majority of the red PDA gradually change colour to blue on cooling to the temperature of liquid nitrogen. However, these transitions are not phase transitions, in contrast to those in the high-temperature range.

It is noteworthy that there is one exception here. The DCHD single crystal undergoes a first-order phase transition

at atmospheric pressure and a temperature of 142 K with a sharp colour change[167]. At this temperature the crystal contracts along the *b* axis by approximately 8% and its density increases by approximately 5%¶. Owing to the large change in density at the phase transition point, the transition is very sensitive to pressure: its temperature increases by approximately 300 K at a pressure of 300 MPa.

Table 4. The thermochromism of poly-*n*ACMU with the substituents R = R′ = $(CH_2)_nOCONHCOO(CH_2)_mH$.[33]

Polymer	*m*	*n*	Temperature of colour transition, °C	
			gold-green → red	red → yellow
Poly-4BCMU	4	4	112	136
Poly-3BCMU	4	3	160	183
Poly-4ECMU	2	4	118	137
Poly-3ECMU	2	3	192	—

[11] См. *Rehwald W., Vonlanthen A., Meyer W.* Phys. Stat. Solidi 1983, B. A75, S. 219.

Soluble PDA have been obtained from DA with urethane substituents. Depending on the changes in the external conditions (temperature, solvent, pH of the medium), numerous phase transitions, called a "transition tree", have been obtained for solutions of these polymers[166]. The total number of transitions involving a colour change is approximately 15. In the series of soluble PDA, the colour transitions have been most thoroughly investigated for poly-*n*ACMU[33,120,167].

The solvatochromism of solutions of these polymers has been investigated under the conditions of changes in the solvent/non-solvent volume ratio, for example, the chloroform/hexane ratio[33,89,120,121,162,167]. The colour of a solution of poly-3BCMU in pure chloroform is yellow. When hexane is added in an amount sufficient to give a composition with 75 vol.% of chloroform, the colour remains unaltered. On further decrease of the relative content of chloroform to below 75 vol.%, there is a sharp colour change to blue and a blue precipitate is deposited (the colour changes are sharp, so that the titration method can be used). The maximum in the absorption spectrum of poly-3BCMU shifts from 21300 cm^{-1} (yellow solution) to 15900 cm^{-1} (blue solution)[167]. The absorption maximum of the blue solution (15900 cm^{-1}) constitutes the absorption limit for a polyene and PDA of infinite length[96]. Analogous colour changes have been observed for a solution of poly-TCDU[168]. Detailed studies of the solvatochromic transitions of poly-3BCMU in a chloroform/hexane mixture showed[91] that the solvent/non-solvent ratios at which colour changes occur differ in the forward and reverse titrations.

Another possible way of influencing the colour of the solutions is by altering the pH of the medium for water-soluble PDA with the substituents $(CH_2)_nOCONHCH_2COO^-K^+$ (n = 3,4) and $(CH_2)_nCOO^-K^+$ (n = 1,2).[169,170] When the pH changes from 9 to 3, the colour of the solution changes from yellow to red or purple.

¶ See D.Bloor, I.F.Chalmers, R.J.Kennedy, and M.Motevalli, Mol.Cryst.Liq.Cryst., 1983, **93**, 215.

An isosbestic point is frequently observed for the thermochromic and solvatochromic transitions, indicating the absence of intermediate products in transitions between two forms of different colour[161,162,169].

It has been suggested that the solvatochromic transitions in PDA solutions have the following cause. In a "poor" solvent or a weak electrolyte, the macromolecules have a planar arrangement of their skeleton, which is additionally stabilised by intramolecular hydrogen bonds (see Fig.8). When a "good" solvent is added or with increase of the concentration of ions in solution, these bonds are ruptured and the planar conformation breaks down, which leads to an alteration of the optical properties[120,121,161,167]. The hypothesis of the existence of planar PDA chain conformations has been confirmed experimentally by viscometric[91] and light scattering[92] methods. The conformational changes lead to statistically distributed breaks in the conjugation chain when the polymer skeleton rotates relative to single bonds and a distribution with respect to effective conjugation lengths l_{eff} arises[121]. Comparison with the spectra of model conjugated molecules has led to the estimate $l_{eff} \gtrsim 30$ repeat units for blue PDA (600 nm < λ_{max} < 700 nm), 20 < l_{eff} < 30 for red PDA (500 nm $\lesssim \lambda_{max} \lesssim$ 600 nm), and l_{eff} < 6 for yellow PDA (400 nm $\lesssim \lambda_{max} \lesssim$ 500 nm)[8].

The method of photoselection with the aid of Raman scattering was used to justify this hypothesis experimentally[171,172]. It is assumed that one conformationally disordered polymer chain consists of a set of chromophores differing in l_{eff} and having as a result different vibrational spectra. The observed absorption band consists of an inhomogeneously broadened line with contributions due to different chromophores. Analysis of the line shape in different solvents where PDA has different colours made it possible to determine the distribution of l_{eff} for the same polymer having, however, different conformations.

Evidently the thermochromic transitions in the crystallised state of PDA cannot be explained by changes in the conformations of the macromolecules. The initial explanation of the thermochromism was based on the hypothesis that this phenomenon is associated with transitions between the mesomeric structures (A) and (B) in the polymer chain[117,118,158]. Indeed the optical absorption spectrum of poly-ETCD at a temperature below the transition point resembles the spectrum of poly-TS for which the structure (A) of the polymer chain has been established. Above the transition point, the spectrum of poly-ETCD resembles that of the poly-DCHD, which has a structure of type (B).

Another view on the cause of the changes in the optical properties of PDA involves the hypothesis that they are determined by the strain in the macromolecular chain and hence by its deformation[173]. Similar deviations from equilibrium bond lengths in a conjugated polymer chain arise owing to interactions of the substituents. The absorption energy of "free" PDA in solution in the equilibrium conformation is approximately 2.4 eV. The smaller value observed in films and crystals is due to the stress applied to the polymer chain as a result of intramolecular and (or) intermolecular interactions of the side groups[4]. The most important causes responsible for the position and form of the optical absorption band are, firstly, the statistical (time-average) deformation of the polymer skeleton and, secondly, dynamic deformation. Whereas the first cause determines the position of the band and its inhomogeneous broadening, the second determines the homogeneous (temperature-dependent) band width. A large inhomogeneous band width can be observed in highly strained or disordered systems[173] and the change in optical absorption takes place owing to the homogeneous band broadening[93]. In other words, it is assumed that the

conjugated PDA chain is rigid and does not undergo conformational changes, while alteration in external conditions leads to the appearance of only a gradual deformation of the bond lengths in the chain. It may be that the thermochromic transitions in the solid PDA are associated with the trans-orientation or a change in the packing of the substituents, which leads to the deformation of the conjugation chain and changes in the electronic structure and colour.

Apart from the thermochromic and solvatochromic phenomena described above, there are a series of physical and chemical transformations of DA and their polymers accompanied by a change in colour[8]. These include the fusion of PDA, the extraction of the monomer from partly polymerised DA, and others. A correlation is almost always observed between the number of methylene groups N_{CH_2} joining the DA triple bond to the functional group and the observed colour transition. For example, in the extraction of the monomer from partly polymerised DA, red specimens with $N_{CH_2} = 1$ and 2 remain red, while blue specimens with $N_{CH_2} = 1,2,4$ become red ($\lambda_{max} = 530 \pm 10$ nm). Thus, regardless of the initial colour, the extraction of the monomer leads to the appearance of a red colour. On the other hand, the extraction of the solvent from partly polymerised DA with $N_{CH_2} = 3$ does not affect the colour. Apart from the colour changes, a correlation has been observed between the number of methylene groups and the solubility and fusibility of PDA[8]. Almost all PDA with $N_{CH_2} = 1$ are infusible and decompose on heating without melting; they are also insoluble in the usual organic solvents. An increase in the number of methylene groups leads to an improvement of fusibility and solubility. Almost all PDA with $N_{CH_2} = 4$ melt and the majority of them are soluble.

(b) Fluorescence

Like the model long polyenes, fully polymerised PDA specimens do not fluoresce. The exceptions are the radiation-polymerised BPG[125], PDA with defects[125,174,175], certain soluble PDA[169,170], and also PDA with chiral substituents in only one of the reactive phases[121].

The causes of the absence of fluorescence of the fully polymerised specimens are obscure, but they can be as follows[168]: (1) the high efficiency of the absorption of the emitted light quanta (reabsorption of light) owing to the small depth of penetration by light which is only 10–100 nm; (2) non-radiative processes in the deactivation of excitation; (3) the transmission of excitation to low-lying energy states from which emission takes place but which have not so far been detected experimentally; rapid intersystem crossing to a triplet level, whose energy is less than half the width of the forbidden gap, and subsequent non-radiative decomposition with emission of phonons may constitute this process.

Some of the monomeric DA are phosphorescent. For example, DCHD phosphoresces with a well-resolved spectrum corresponding to emission from four traps, whose depths are 2.8, 8.7, 27.8, and 45.7 meV.[68] It has been assumed[68] that these traps are populated and liberated via a triplet exciton band. Direct emission from this band cannot be detected for some reason. The arrangement and concentration of the traps are not random, since the ratio of the phosphorescence band intensities is the same for different specimens. The time of emission from the traps is less than 7 s. It has been suggested that the traps have a triplet spin polarisation.

Almost nothing is known about the nature of the broad fluorescence bands of the DCHD monomer. From the instant of the beginning of polymerisation, both the phosphorescence and fluorescence are fully absorbed by the conjugated polymer skeleton[176]. Certain partly polymerised PDA do fluoresce. Thus the partly polymerised TS specimen gives rise to a fairly satisfactory fluorescence spectrum[175]. On excitation with light (at 4.2 K), two emission bands were observed at 20486 and 20802 cm^{-1} accompanied by vibrational side bands. The emission band frequencies are displaced by approximately 4000 cm^{-1} towards shorter wavelengths relative to the optical absorption edge of the polymer. Furthermore, four additional emission bands are observed whose wavenumbers $\tilde{\nu}_{fl}$ are related to the wavenumber of the exciting light $\tilde{\nu}_{exc}$ by the simple expression $\tilde{\nu}_{fl} = \tilde{\nu}_{exc} - \tilde{\nu}_i$, where $\tilde{\nu}_1 = 988.7$, $\tilde{\nu}_2 = 1227$, $\tilde{\nu}_3 = 1513$, and $\tilde{\nu}_4 = 2085$ cm^{-1}. The ν_i were assigned to the vibrational energies of the excited state of the fluorescent centre. It is surprising that these quantities, which refer to an excited state, agree well with the vibrational energies of the ground state of the chain observed with the aid of Raman spectroscopy: 955, 1205, 1487, and 2088 cm^{-1}.[177]

The spectroscopic characteristics of the fluorescence of the partly polymerised poly-TS are independent of the type of specimen (single crystal, polycrystalline material, or powder). The observed fluorescence is attributed to the geometrically and energetically localised states. The concept of geometrical localisation arose owing to the dependence of the fluorescence intensity on the position of the laser spot of the exciting light on the surface of the crystal. On passing from one irradiated site to another, the fluorescence intensity can then change by a factor of 100 and the maximum intensity is observed when the boundaries between the crystals are irradiated. The energetic localisation is understood as the absence of an energy linkage between the fluorescence centres and the polymer chain[174].

In order to elucidate the role of defects in fluorescence, a study has been made[174] of a specially prepared poly-TS specimen with a large number of defects[174]. The absorption spectra recorded at 4.2 K showed new (relative to the defect-free specimen) bands; two narrow bands (at 20665 and 21050 cm^{-1}) and two broad bands (at 20500 and 20830 cm^{-1}). The positions of the last two bands coincide with those of the fluorescence bands. It is not clear why fluorescence is observed for only one of the pairs of bands observed in absorption.

As regards the nature of the fluorescent centres, it has been suggested that they may consist of triplets at the end of the polymer chain which have become frozen in the ground state. In this case the absorption and fluorescence are associated with the allowed $T-T$ transition[175]. The fluorescence of solutions is determined by sections of the polymer with disrupted chain conjugation[169].

(c) Non-linear Optical Properties

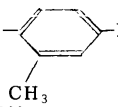
The tensor molecular polarisability $\mathbf{P}$ and the applied electric field $\mathbf{E}$ are linked by the relation $\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3$, where $\chi^{(1)}$ is the coefficient of the linear optical susceptibility and $\chi^{(2)}$ and $\chi^{(3)}$ are the coefficients of the non-linear second- and third-order optical susceptibilities respectively. For centrally symmetrical molecules, to which the vast majority of PDA belong, $\chi^{(2)} = 0$. In calculations based on the perturbation theory using the free electron model, $\chi^{(3)} \propto L^5$, where L is the length of the conjugation chain in the linear molecule[178], while in calculations based on the π-electron approximation $\chi^{(3)} \propto N_d^6$, where N_d is the electron localisation parameter[179]. It has been shown experimentally that $\chi^{(3)}$ does not increase with increasing conjugation chain length as rapidly as predicted by the theory. The

explanation is that the real electron potential is periodic, for example, owing to the alternation of the bond lengths, the degree of delocalisation of electrons is therefore smaller than in the free electron model[178].

The non-linear optical susceptibility coefficient is fairly high for PDA single crystals. Thus $\chi^{(3)} = 7 \times 10^{-11}$ CGS units for poly-TCDU and $\chi^{(3)} = 8.3 \times 10^{-10}$ CGS units ($\lambda = 1.89$ μm) for poly-TS.[178,180] The electrical breakdown parameter for PDA is very high. For poly-TCDU it is 50 GW cm^{-2} in the picosecond range, which is higher by a factor of 20 than for germanium. If one considers the quality parameter defined as $\chi^{(3)}/n^2$ (n is the refractive index), the latter is found to be 1.1×10^{-11} for poly-TCDU and 4.5×10^{-10} for poly-TS, compared with, for example, 2.5×10^{-11} for germanium and 0.45×10^{-11} for gallium arsenide (all the values are expressed in CGS units). Multilayers based on DA also possess non-linear optical susceptibility†. $\chi^{(3)} = (0.67 \pm 0.20) \times 10^{-12}$ CGS units for the ammonium salt $CH_3-(CH_2)_{17}-C\equiv C-C\equiv C-COO^-NH_4^+$, which yields $\chi^{(3)} \cong 1.34 \times 10^{-11}$ CGS units when account is taken of the degree of conversion.

The non-linear optical properties of solutions of poly-3(4)BCMU have been investigated by the method of three-wave mixing, in which two light beams from laser sources with frequencies ω_1 and ω_2 were directed onto the specimen and the generation of light with the frequency $\omega_3 = 2\omega_1 - \omega_2$ was observed[181-184]. It was found that there is a large contribution by the direct two-photon absorption with a cross-section β to the third-order non-linear optical susceptibility coefficient. The value obtained for a solution of poly-4-BCMU is $5 \times 10^{48} \lesssim \beta \lesssim 10^{-46}$ cm^4 s photon^{-1} (chain unit)$^{-1}$, which is the highest known value, much greater than, for example, that for CS_2, where $\beta \cong 5 \times 10^{-49}$ cm^4 s photon^{-1} molecule^{-1}.

The occurrence of the two-photon absorption and its large cross-section can limit the application of PDA as active elements in non-linear optics. On the other hand, studies of poly-TS and poly-TCDU single crystals have led to the hypothesis that the observed absorption is not a two-photon process and is more likely to be a two-stage process: the absorption of the first photon creates a defect in the conjugation chain, for example, by transition of an electron to a localised orbital; the absorption of the second photon is associated with a transition whose initial or final state is a newly formed defect[185]. Subsequent experiments should provide an answer to the question of the role of the two-photon absorption and its nature and hence of the practical value of PDA from the standpoint of their application in non-linear optics.

In order to expand studies on the non-linear optical properties of PDA and of their possible applications, asymmetric DA[186,188] and DA with chiral substituents[21,189] have been synthesised. The generation of a second harmonic has been observed for DA with R = CH_2NH–  –NO_2 and R′ = $(CH_2)_8CONHC_2H_5$ and its polymer[188]. The possibility of using multilayers based on PDA in integrated non-linear optics and also in light guides has also been considered[190].

VI. ELECTRON PARAMAGNETIC RESONANCE IN POLYDIACETYLENES

During the polymerisation of diacetylenes, considerable changes take place in the EPR spectrum. In the initial polymerisation stage several lines are observed, many of which are characterised by the anisotropy of properties as a function of changes in the mutual orientations of the external magnetic field and the crystal[46]. As polymerisation reaches completion, the number of lines and the overall paramagnetic susceptibility diminish until a single weak signal, characteristic of all polyconjugated systems, remains when almost 100% conversion of the monomer is reached[48]. Such a change in the EPR spectrum on polymerisation is explained by the fact that in the initial polymerisation stage the main contribution to absorption comes from the active species at the end of the growing chains, while after the completion of polymerisation the EPR signal is determined by the paramagnetic species bound to the polymer chain. In conformity with such subdivision, the study of the EPR parameters in the initial polymerisation stage can yield information about the polymerisation kinetics and about the structure of the active centre propagating the chain, while the conformational structure of the polymer chain can be investigated by studying the EPR spectrum after the end of polymerisation.

The observed EPR spectrum in the initial polymerisation stage can be described by the spin Hamiltonian $H = \mu_B \mathbf{BgS} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2)$.[46] The g-tensor is almost isotropic and its principal values hardly differ from the g-factor of the free electron. The splitting parameters at zero field on polymerisation of TS and BPG are very similar and amount to $D/hc \cong 0.26-0.27$ cm^{-1} and $E/hc \cong -0.05- -0.08$ cm^{-1}, which indicates the identical mechanism of initiation and the identity of the paramagnetic centres active in polymerisation. The smallness of the parameter E shows that the distributions of the spin density of the carbon atom in the sp-hybridised state along the x and y axes are approximately equally probable.

In the ultraviolet-initiated polymerisation a number of lines in the EPR spectra and the range of variation of the zero field splitting parameters increase. For example, lines due to nine non-equivalent triplet centres have been observed for TS and the following values have been obtained for them: 0.275 $cm^{-1} \leq D/hc \leq 0.367$ cm^{-1} and -0.008 $cm^{-1} \leq E/hc \leq -0.006$ cm^{-1}.[76] The study of the dependence of the line intensities in the EPR spectrum and of the zero field splitting parameters on the degree of polymerisation together with a parallel investigation of the optical properties made it possible to reach well-founded conclusions concerning the nature of the initiating species in the structure of the active polymerisation centres. During the ultraviolet polymerisation of BPG, optical spin polarisation is observed[191]. The proposed mechanism of this phenomenon consists in the absorption of light (280 nm $\leq \lambda \leq$ 370 nm) by the benzene ring of the substituent and the subsequent triplet energy transfer to the conjugated chain via intersystem crossing $S_1 \rightsquigarrow D_0$, where S_1 is the excited singlet state of the benzene ring of the substituent and D_0 the triplet state of the DA molecule. As a result, two new emission lines are observed in the EPR spectra. Optical electronic spin polarisation ($\lambda < 590$ nm) is observed also for the ground triplet state of the poly-TCDU chain having the structure ~CR–RC=C–C≡CR.[88] The authors explain this phenomenon with the aid of a Jablonski diagram.

As polymerisation proceeds, the intensity of the high field lines, characteristic of the triplet state, diminishes until the ultimate disappearance of the lines at the end of the rapid stage of the reaction. After the completion of polymerisation, a single line remains with a g-factor close to that of the free electron. As in the discussion of the mechanism of the formation of paramagnetic centres in polyconjugated systems, it has been suggested that the paramagnetic properties of PDA are determined mainly by the delocalised structural

† See F.Kajzar and J.Messier, Thin Solid Films, 1983, **99**, 109.

defects of the polymer chain[114] which can have, for example, the following structure:

$$\sim\!=\!RC\!-\!C\!\equiv\!C\!-\!\dot{C}R\!-\!RC\!=\!C\!=\!C\!=\!CR\!-\!RC\!=\!C\!=\!C\!=\!CR\!-\!R\dot{C}\!-\!C\!\equiv\!C\!-\!CR\!=\!\sim\ .$$

It is easy to represent different mesomeric forms of this biradical which correspond to the migration of the free spin along the chain. It is less likely that the paramagnetism is due to inactive radicals at the ends of the growing polymer chains[47].

The parameters of the EPR signal in the fully polymerised PDA specimens are very similar to the known characteristics of the EPR signals for other polyconjugated systems. In particular the g-factor is $g = 2.0023 \pm 0.0002$,[46] the line form at the centre is Lorentzian, the wings have the Gaussian shape[16,46], and the line width, measured between the points of maximum slope, varies from 5 G for poly-TS[46] to approximately 10 G for poly-HD.[16] The concentration of the paramagnetic species depends on the nature of the monomer and amounts to 1.6×10^{17} spins g^{-1} for poly-HD[36] and 8×10^{15} spins g^{-1} for poly-TS.[48] As for other polyconjugated systems, the EPR signal of PDA is readily saturated for low UHF field powers and a relation is observed between the intensity of the EPR signal and the degree of crystallinity (the degree of packing in the case of polyconjugated systems): the greater the degree of crystallinity, the lower the concentration of paramagnetic centres[192].

As for polyconjugated systems, in the case of PDA the previous history of the specimen is found to influence the behaviour of the EPR parameters. This is apparently associated with the slow relaxation of the internal stresses in the crystal and the consequent change in the number of paramagnetic defects in the chain due to this process. A narrow EPR signal ($\Delta B = 0.9$–1.2 G) has been observed for poly-TS in addition to the usual EPR signal[192]. Irradiation of a PDA specimen having $R = CH_2OH$ and $R' = CH_3$ by light at a wavelength $\lambda \cong 700$ nm results in the observation of a narrow signal (< 3 G) in the "tail" of the optical absorption. This signal is of unknown origin, appearing and disappearing reversibly at all temperatures from liquid helium temperature to room temperature. Its lifetime amounts to hours at 4.2 K and seconds at 30 K.[5]

The study of the temperature variation of the EPR signal intensity in poly-TS led to the following results[193]. In the range 90–220 K the paramagnetic susceptibility obeys the Curie law, which indicates a constant density of defects in this temperature range, provided that the PDA paramagnetism is attributed to structural defects. Activated processes, leading to an increase of the number of paramagnetic species, begin above 220 K. In the temperature range 233–353 K the EPR signal intensity is given by the expression $\chi'' = \chi_0''[\exp(-\Delta E/kT)]h\omega/2kT$, where $\Delta E = 75 \pm 25$ meV; this quantity is thought to be related to the activation energy for the formation of mobile paramagnetic defects[46]. The product of the spin–spin and spin–lattice relaxation times T_1T_2 was measured in the same temperature range and it was established that at 250 K there is a fairly sharp change in the law governing the temperature variation of the product of the reciprocals of the relaxation times: $1/T_1T_2 \propto T^{1.8}$ at temperatures below 250 K and $1/T_1T_2 \propto T^{9.3}$ above 250 K, i.e. there is apparently a change in the relaxation mechanism from the direct mechanism at low temperatures (the theoretical power exponent of the temperature is $n = 2$) to a two-phonon Raman mechanism ($n = 9$). Below the transition temperature, the molecular movements of the chains are "frozen", whereupon their densest packing is attained and the number of chain defects is constant. Above this temperature the mobility is "unfrozen" and the number of defects is determined by the temperature. It is apparently not fortuitous that a phase transition associated with the reorientation of the substituents is in fact observed in this temperature range[126,135,138,140,141].

The overall experimental results indicate the dependence of the EPR signal parameters on the nature of the initial monomer, the method used to isolate the polymer, and the previous thermal and morphological history of the specimen[194]. Thus the EPR signal intensity during polymerisation at conversions > 10% can either decrease (TS)[114] or increase (HD)[16]. Such behaviour is attributed to the different degrees of strain in the polymer chains formed, which is greater in the case of HD[16]. This is also indicated by the greater width of the absorption line for HD. It has likewise been suggested that only a small proportion of all the chain defects are paramagnetic while the majority are non-paramagnetic and the chain defects are attributed to the transition from the non-paramagnetic strained state of the polymer chain to a state having a lower energy with breakdown of the conformation and the formation of paramagnetic defects[192]. Different defects, allowed by the topology and symmetry, have been considered theoretically[195].

VII. ELECTROPHYSICAL PROPERTIES OF POLYDIACETYLENES

In terms of their absolute dark conductivity, the PDA are dielectrics. The dark conductivities of polymers obtained from different initial monomers vary from 10^{-16} to 10^{-10} Ω^{-1} cm^{-1}.[69,127,128,196] According to the kinetic analysis of the carriers, the dark conductivity of PDA is due to the ionisation of impurities.[197] Indeed, the dark current is determined by the quality of the crystal and the time for which it is maintained *in vacuo* before the measurements and varies from specimen to specimen. For example, the decrease of the dark conductivity on passing from measurements in air to measurements *in vacuo* amounts to several orders of magnitude[10].

It was later established that the dark conductivity, which obeys Ohm's law like the dark current limited by the space charge, is determined by the localised levels at distances of 0.80 ± 0.02 eV from the edge of the band and their concentration, which corresponds to $\lesssim 1$ centre per meter of the length of the polymer chain[198]. The level with an energy of 0.80 eV functions as the donor for the Ohmic dark conductivity and as a trap for the injected carriers. For all the orientations of the polymer single crystal relative to the external electric field and under all conditions of study, the dark current obeys the law $i \propto \exp(-\Delta E/kT)$, where $\Delta E = 0.80$ eV. The sign of the carrier could not be determined.

By analogy with the familiar results obtained for the doping of polyacetylene, the PDA specimens were also treated with halogen vapours[199]. Thus polyhexa-2,4-diyn-1-ol absorbed iodine vapour in an amount up to 1.2 atoms per unit, forming a lustrous black material. The dark conductivity increased by 6–7 orders of magnitude and in terms of its increment the effect proved almost the same as for $(CH)_x$. The colour of polyocta-3,5-diyne-1,8-diol did not change and its weight did not increase on treatment with iodine vapour or solution, which can be explained by the dense molecular packing of the hydrogen-bonded macromolecules. The diffusion of the large iodine molecules between such macromolecules is greatly hindered. The doping with iodine was carried out for two-layer poly(diacetylenecarboxylic acid) films. In this case the increase of the dark conductivity is not so great and σ increases from 10^{-10} to 10^{-7} Ω^{-1} cm^{-1}. The increase of the conductivity is reversible: after the removal of iodine, the conductivity returns to its initial value[200]. Somewhat better

results were obtained when the doping was carried out before polymerisation. For example, the specific conductance $\sigma = 10^{-4}\ \Omega^{-1}\ cm^{-1}$ was obtained for the TS crystal doped with iodine and polymerised at room temperature[201]. Analogous investigations have been carried out for other DA and the influence of various factors on the specific conductances of the doped polymers was studied.

Numerous studies have been devoted to the photoconductivity of PDA. It was established as a general rule that the maximum on the spectral photoconductivity curve is always displaced towards higher energies relative to the maximum in the optical absorption spectrum. The absolute photocurrent in PDA depends greatly on the nature of the monomer and can vary by several orders of magnitude[2,10,117]. The yields of the photocurrent carriers of both signs are the same, which indicates their dipolar generation[202]. An approximately linear dependence of the photocurrent on the exciting light intensity has been observed[127]. Like other physical properties, the photoconductivity is found to be anisotropic: for light polarised parallel to the chain, the photocurrent is approximately 10 times[158] and the quantum yield in the formation of the carrier is approximately 100 times[203] greater than for the light polarised at right angles to the chain. The ratio of the photocurrent to the dark current at 300 K is approximately 300; it increases with decrease of temperature to approximately 600 at 120 K for an electric field strength of 1300 V cm^{-1}.[127]

The mobility of the carriers, one of the most important characteristics of photoconductors, is unusually high for organic materials and, according to data obtained by different methods for different specimens, varies within wide limits: from 1–5 $cm^2\ V^{-1}\ s^{-1}$ [202–206] to 10^2,[207] 2.8×10^3,[133] 6×10^3,[208] and even $2 \times 10^5\ cm^2\ V^{-1}\ s^{-1}$.[209] The mobilities calculated by quantum-chemical methods are $10^3\ cm^2\ V^{-1}\ s^{-1}$ [97] and $1.7 \times 10^3\ cm^2\ V^{-1}\ s^{-1}$.[107] Other workers[206–210] continue to adopt for the mobilities values in the range 1–10 $cm^2\ V^{-1}\ s^{-1}$. More careful experiments and the theoretical consideration of the mechanism of the formation of the current carriers and the associated kinetics should indicate the true mobility and the causes of such large discrepancies between the experimental values.

Like other physical properties, the mobility is anisotropic $\mu_\parallel / \mu_\perp = 10^2–10^3$.[128,198,203,204] An even greater anisotropy ($> 10^4$) has been found for the microscopic mobility#. The rate of drift of the carriers is in the range from 240 m s^{-1} [204] to 900 m s^{-1},[202] while another study[209] yielded an unexpected result, namely that the rate is constant at 2×10^3 m s^{-1} and is independent of the electric field strength down to the lowest values ($E < 1$ V cm^{-1}) and is comparable to the estimated velocity of sound (5×10^3 m s^{-1}).[42]

According to various estimates, the lifetime of the carriers ranges from $10^{-6}–10^{-8}$ s[128,202,205] to 10^{-13} s.[133] Owing to the differences between the estimated mobilities and lifetimes of the carriers, the estimated length of the free path varies within a wide range: from approximately 10 nm for monolayers and multilayers of cadmium polydiacetylenecarboxylate salts[211] to 1 mm in a single crystal of poly-TS.[207,209] The latter value is in surprisingly good agreement with the average length of the unaffected sections of the polymer conjugation chain (0.1–1 mm) obtained from the measured density of dislocations ($\sim 10^{13}$) m^{-2})[212] and, provided that this agreement is not fortuitous, the length of the free path is limited solely by the dislocations in the single crystal which serve as traps for the carriers. The average length of the carrier path between interactions with acoustic phonons has been estimated as 8 μm.[209] The effective mass of the carrier is surprisingly small ($m^* = 0.05m_0$) for organic crystals[133].

In the study of photoconductivity over a wide range of energies of the light quanta (from 0.62 to 3.1 eV), the principal qualitative characteristics of the behaviour of the spectral curve were elucidated.[207,213] One of the main features proved to be a rapid decrease of photoconductivity at $\hbar\omega < 0.8$ eV, which is consistent with data[198] indicating the existence in PDA of localised impurity levels with the same energy. The spectral photoconductivity curve can be divided into three regions: (1) in the region where $\hbar\omega < 2.0$ eV, photoconduction takes place as a result of the ionisation of impurities; (2) in the region where $2.0 < \hbar\omega < 2.4$ eV, it arises as a consequence of the exciton absorption with subsequent autoionisation of excitons; (3) in the region where $\hbar\omega > 2.4$ eV, direct generation of current carriers in an interband transition is observed. The quantum efficiency of the irradiation is high in the first and third regions and is small in the second region. The photoconductivity maximum in the first region at 1.64 eV[197] is fairly difficult to account for. Nor is it clear whether or not it is fortuitous that the energy of this maximum is approximately equal to twice the energy of the traps.

The one-dimensional conductivity model is valid for the current flowing along the polymer chain[213–217]. According to its electronic properties, PDA belong to the class of semiconductors with broad bands. The existence of bands with a width amounting to several electron-volts has been established for these substances with the aid of calculations and electronic spectroscopy for chemical analysis (ESCA) and electron injection[208] and photoemission[218] methods. However, it is not clear how these results can be reconciled with the high mobility of current carriers observed for PDA which is characteristic only of semiconductors with narrow bands.

Compared with many polymers having conjugated bonds, the PDA have fairly weak electrophysical characteristics. There are several reasons for this. Firstly, the structure of the chain in these polymers is significantly one-dimensional, which leads to the effective recombination of the carriers located on one chain and their consequent low concentration. Indeed not more than two carriers per polymer chain have been observed[209]. Secondly, a pure PDA single crystal contains a very small number of impurities and defects, so that the impurity conductivity is low. Thirdly, a characteristic feature of the optical absorption of PDA is that the probability of the transition to the exciton levels is much higher than that of the direct interband transition. The exciton states lie approximately 0.5 eV below the bottom of the conductivity band and their lifetime is very short. The probability of the thermal ionisation of excitons with formation of free carriers is therefore negligible. These factors create serious difficulties for the practical employment of PDA as photoconductors.

On the other hand, the mobility of the carriers in PDA is very high. Therefore, if it were possible to create a high concentration of carriers (one of the obstacles to this is the one-dimensional character of the polymer chain), one might hope to obtain high electrophysical characteristics of PDA. Another way of increasing the photoconductivity involves the sensitisation of the photoconduction either by means of chromophores constituting a component of the side substituents in the PDA chain or by introducing chromophores capable of cocrystallisation with the DA monomers and the subsequent formation of PDA. In both cases it is possible to achieve a location of the chromophores which is the closest possible to the polymer chain in order to ensure the

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See U.Seiferheld, B.Ries, and H.Bässler, J.Phys., C., Solid State Phys., 1983, **16**, 5189.

most effective charge transfer. Furthermore, the introduction of chromophores must not hinder the solid-phase polymerisation and the electronic structure must promote most effectively the sensitisation of the photoconduction in PDA. The first attempt of this kind was undertaken in a study of the photoconductivity of poly-DCHD containing carbazole side groups[219].

It may be that an improvement of the electrophysical properties can be attained by employing isostructural doping (i.e. doping which does not alter the structure of the PDA crystal or multilayers).

VIII. RAMAN SPECTROSCOPY OF POLYDIACETYLENES

The application of the Raman spectroscopic method to the study of PDA is one of the examples illustrating the extensive possibilities of this method[6]. In contrast to other procedures, Raman spectroscopy can yield direct information about the bond sequence in the polymer, about the degree of their strain, and about the influence of the surrounding monomer matrix on the growing polymer chain[4,5]. Despite the fact that, according to the results of analysis, the total number of vibrations active in the Raman spectrum of PDA is fairly large, only a small proportion of such vibrations are enhanced by resonance, which results in a considerable simplification of the Raman spectra. This can be explained by the fact that the intense optical absorption observed in the visible region owing to the excitation of the π-electron conjugation system in the polymer chain leads to the resonance enhancement of only those vibrations which induce the modulation of electron density along the chain. The resonance enhancement effect is so large that Raman spectra without noise can be recorded for only 20 DA monolayers[220] or for a degree of conversion of the monomer much less than 1%.[221] The normal vibrations of the main chain, which do not induce the modulation of the electron density along the chain, and the vibrations of the side groups are almost inactive in the Raman spectra.

Between four and nine bands in the range 600–2200 cm^{-1} have been observed in the Raman spectra of DA and PDA specimens[177]. The emission is highly polarised for all the bands and the electric field vector is parallel to the direction of the polymer chain[138]. The position and form of the bands depend on the nature of the substituents, the temperature, the mechanical stress applied to the specimen, and the wavelength of the exciting light.

The largest number of studies have been performed for TS and its partly and wholly polymerised specimens. For the fully polymerised poly-TS crystals, only four intense bands are observed in the Raman spectra: $\tilde{\nu}_1 = 2086$, $\tilde{\nu}_2 = 1485$, $\tilde{\nu}_3 = 1203$, and $\tilde{\nu}_4 = 952$ cm^{-1}. The changes in the positions of these lines during polymerisation have been investigated[221]. During the induction period of the polymerisation reaction (degree of conversion of the monomer < 10%), the frequencies in the Raman spectra are independent of the degree of polymerisation. During subsequent polymerisation, the frequencies increase: the shifts of $\tilde{\nu}_1$ and $\tilde{\nu}_2$ are much greater than those of $\tilde{\nu}_3$ and $\tilde{\nu}_4$ and amount, for example, to approximately 60 cm^{-1} for $\tilde{\nu}_1$. In addition it has been established that the polymerisation is spatially inhomogeneous. This is manifested particularly by the broadening of the line, the appearance of additional lines, and by the fact that the intensities and frequencies of the lines are sensitive to the position of the laser beam relative to the surface of the irradiated specimen[221].

The dependence of the frequency shift on the application of external mechanical stresses to poly-TS has been investigated[222,223]. The Raman bands are then displaced towards higher frequencies, while the optical absorption maximum at 2 eV is actually displaced towards lower energies "at a rate" of approximately 8 meV $kbar^{-1}$. Both these results are in satisfactory agreement with predictions based on the molecular orbital method. It has been suggested that the changes in the Raman frequencies during polymerisation and the frequency shift when external mechanical stresses are applied to the specimen have a common basis—namely they are due to the appearance of strain in the polymer chain and the change in the force constants of the bonds.

The thermal polymerisation of MBS, a monomer isomorphous with TS, has been investigated by the Raman method[19,63]. The positions of the lines in the Raman spectra of MBS virtually coincide with their positions in the spectrum of TS, although the initial molecular strain in the polymer chain of MBS is greater. This excess strain is, however, eliminated in the very early stages of the polymerisation of MBS because of the easier, compared with TS, reorientation of the side substituents, which leads to a longer lifetime of the active centre and to a higher pre-exponential factor, which determines the significant difference between the kinetic curves for the polymerisation of TS and MBS.

Other DA have also been investigated by the Raman method. The spectra of the partly and fully polymerised BPG have a greater number of bands than that of TS[125], which can be explained by the presence of structures without a centre of symmetry, by the Fermi resonance interactions, or, finally, by vibrations in the substituents linked to the polymer skeleton. The frequency shifts in the Raman spectra of BPG on passing from the monomer to the polymer are greater than for TS.[224]

In contrast to poly-TS, the frequencies of the Raman lines of poly-HDU subjected to stretching stresses decrease linearly with increase in the length of the specimen[225]. It has been demonstrated by Raman spectroscopy that the phase transition in DCHD is due to a rearrangement of the side groups, which leads to an alteration of the strain in the crystal[160]. The frequency shift following the introduction of phenazine into the cocrystallising composition with diacetylenemonocarboxylic acid is small, indicating an effective cocrystallisation which does not give rise to additional strains[34].

A very intense narrow line has been observed in the Raman spectrum following the absorption of O_2 molecules on the surface of the single crystals of certain PDA[226]. The resonance enhancement occurs in this instance owing to the considerable energy transfer from the conjugated skeleton to the O_2 molecule in the electronic transition in PDA with an energy of 2.39 eV. The Raman frequency $\tilde{\nu} = 1521$ cm^{-1} has been obtained for a poly-TS single crystal.

Because of the large number of observed bands due to the functional side groups in the infrared spectra of diacetylenes and their polymers and the difficulty of interpreting these lines, studies have been performed only in the near infrared ($\tilde{\nu} = 3500–12000$ cm^{-1})[227] and the far infrared ($\tilde{\nu} = 5–120$ cm^{-1})[143].

IX. OTHER EXPERIMENTAL METHODS FOR THE INVESTIGATION OF POLYDIACETYLENES

Polydiacetylenes have fairly good mechanical properties. For example, the tensile strength of poly-HDU is approximately 1.7×10^7 Pa, while the dynamic modulus is approximately 4.7×10^6 Pa.[228] If the modulus is calculated per PDA

molecule, its value is almost the same as for diamond. The maximum disruptive stress depends on the size of the specimen: it is greater, the smaller the crystal, which indicates the decisive role of dislocations or other defects in the breakdown of the specimen. The anisotropy of the mechanical properties of PDA is very pronounced[229]. The mechanical properties have been examined in greater detail by Young and Zachmann[230].

The temperature coefficient of the linear expansion α for the PDA investigated is negative over a wide temperature range 231–233, which have been attributed mainly to the increase of the amplitude of the torsional vibrations as the temperature increases and with decrease of the length of the polymer chain due to this effect. The typical values of α are -10^{-5}– -10^{-6} K^{-1}.

The specific heats of a poly-TS single crystal and their temperature variation have been determined in the temperature range from 3 to 300 K.[144] The experimental results are described satisfactorily by the long chain model involving the presence of acoustic and optical phonons.

A pyroelectric effect has been observed for poly-TS[155,234], which is extremely strange, since theory predicts its existence only for molecular crystals without central symmetry. The measurements are performed along the *b* axis, the pyroelectric constant changes sign several times as the temperature is varied, and its maximum value is approximately 10^{-10} CGS units. Pyroelectric properties have also been observed for other PDA.[235]

The ^{13}C NMR method has been used to study solutions of poly-3(4)BCMU[93,236] and it has been established that these polymers have the (A) structure of the chain and that in the gel state the chain has a rigid planar conformation.

The ESCA method has been used to determine the positions and widths of the valence and conductivity bands[237–240]. The ionisation potentials of several of the PDA investigated proved to be similar, amounting to 7 ± 1 eV. Unfortunately the application of the ESCA method is complicated by the considerable contribution of the photoelectrons emitted by the substituents, which precludes the determination of other parameters of the electronic structure of the polymer chain.

In contrast to the ESCA method, the electron photoemission method[218] does not suffer from problems associated with the movement of the charge within the material and the results obtained with its aid may be more reliable. Thus it has been found that the ionisation potential is 7 ± 1 eV, the electron affinity is 5 ± 1 eV, and the width of the forbidden gap is 2.1 ± 0.1 eV. According to the diamagnetic susceptibility measurements, the conjugation in PDA is significantly one-dimensional with a large electron delocalisation region[241].

X. THE POSSIBLE APPLICATIONS OF DIACETYLENES AND POLYDIACETYLENES

The specific features of the reactivity of DA, the characteristics of its structure, and the changes in its physical properties on passing from the monomer to the polymer as well as a number of the physical properties of DA-based polymers determine the possible applications of these compounds.

For example, DA with $R = R' = CH_2OCONH(CH_2)_3CH_3$. .(HDDBU) and $R = R' = CH_2OCONHC_2H_5$ accelerate the radiation-induced cross-linking of polyethylene (PE).[242] The dose in the irradiation of the PE + HDDBU mixture necessary to attain the gel point is smaller by a factor of 15 than for pure PE. The reason why the radiation-induced cross-linking of PE is accelerated only by the DA indicated above consists in the fact that these monomers cocrystallise homogeneously with PE, while others form their intrinsic phase on mixing.

It has been suggested that the numerous colour changes in PDA during its polymerisation be used for the direct visual indication of the previous radiation and thermal history of the specimens[87,243,244]. Both the individual DA and the numerous cocrystallising compositions are very sensitive and visually observable indicators of γ-irradiation doses in the range from 50 rad to 50 Mrad.

The reversible thermochromic transitions in various PDA at temperatures from −180° to 220 °C can be used as temperature indicators and also in indexing devices[245].

Diacetylenes and polymers based on them can be used as indicators of ozone[246], since even small amounts of this gas decolorise the materials by breaking the conjugation chain.

The solubilities of certain PDA as well as their ability to change colour when external conditions are altered made it possible to create on their basis one-component inks and dyes[247].

Cocrystallising compositions made up of HDU and a symmetrical DA with $R = R' = CH_2OCONHC_6H_4Cl$ have been suggested for the recording of fingerprints[248]: polymerisation does not take place on a surface containing traces of fat, while on a clean surface thermal polymerisation occurs with a change in colour from red to violet over a period of approximately 10 min at room temperature or approximately 1 min at 120 °C.

The ability of DA to change colour on polymerisation under the influence of external sources (irradiation with ultraviolet light, γ-rays, and electrons) has led to numerous suggestions for their employment as carriers of information. One can achieve thereby a high density of the recording of information. For example, the resolution attained for a TS single crystal (> 1000 line mm^{-1}) is better than for highly resolving photographic films based on AgBr and photoresistors[249]. Amplitude and phase holograms[249,250], also with a high resolution, have apparently been obtained for the first time for organic crystals on the same TS single crystal. A disadvantage of the TS single crystal is its brittleness. The technology of the employment of DA for the recording of information can be improved by using multilayers[251]. An important advantage of the application of DA for this purpose is the fact that there is no need for a development process in order to obtain an image or information.

The use of DA, particularly of their multilayers, as photoresistors and electronic resistors in lithography is extremely promising. The general requirements which must be met by the materials used for this purpose are a high resolution, high contrast, a high sensitivity, uniformity of the coating, etc.[252] The first results obtained (resolution ~ 50 nm, sensitivity ~ 10^{-6} C cm^{-2}) showed that the employment of multilayer coatings in electronic lithography and photolithography is promising[252–254].

Yet another possibility for the recording and storage of information is provided by the suggestion that multilayers each of which carries an electric charge be used[255]; the charge is photoinjected into a film in a time sequence corresponding to the information introduced, after which it is distributed in space and arranged in order with the aid of a controlling electric field.

The prospects for the application of DA and their polymers in non-linear optics are no less promising. Apart from the high non-linear third-order optical susceptibility coefficient examined above, which is itself important for practical applications, it has been reported[188,256] that a second harmonic of the emission can be generated on the basis of DA and their polymers and that the characteristics are greatly improved compared with those known for inorganic materials,

such as, for example, lithium niobate. It has been suggested that DA and their polymers be used as planar waveguides and other non-linear optical elements[190]; the losses in such waveguides are very small, amounting to 0.01–0.1 dB km^{-1}.[256]

However, one should note that despite the promising predictions as regards the application of DA and their polymers for practical purposes, there exist a number of obstacles to their extensive use. The point is that monomeric diacetylenes can frequently be obtained only as a result of fairly complex multistage syntheses; they must be stored under special conditions (in solution or at low temperatures in the dark); the single crystals must be grown by special methods; it is also difficult to obtain their multilayers. However, the prospects for the employment of DA and PDA are so great and promise so much that these temporary difficulties will undoubtedly be overcome.

XI. MONOLAYERS AND MULTILAYERS BASED ON DIACETYLENES

Problems of the kinetics and mechanisms of the polymerisation and the physical properties and applications of diacetylenes and polyacetylenes were examined above mainly in relation to their single crystals, because the ability to form single crystals is their characteristic feature and determines many of their experimentally observed parameters and properties. In practice, with the exception of several illustrative examples, diacetylenes capable of forming monolayers and multilayers have not been considered. This class of acetylenes has recently attracted special attention in view of the prospects for their practical applications (see Section IX of this review).

The class of diacetylenes capable of forming monolayers and multilayers includes asymmetrically substituted DA, one of the substituents of which is markedly hydrophobic while the other is hydrophilic, and which usually have the structure $H(CH_2)_m-C{=}C-C{\equiv}C-(CH_2)_nCOOX$, where $m,n \geq 0$ and X = H or alkali metal cation. These diynoic acids, transferred from a solvent onto the surface of water, are oriented on the latter in a strictly defined manner. If a support whose surface has been specially treated to increase the extent of its interaction with the hydrophobic end of the DA molecule begins to be immersed in the liquid phase, then the monomolecular DA layer can be "removed" from the surface of water and transferred onto the support with retention of the orientation of the substituents; the diacetylenic bonds are themselves oriented in a specific manner under these conditions. Thus the monolayer on the support has been specially prepared for subsequent topochemical polymerisation. This procedure, involving the transfer of the monolayer from the surface of water onto the support, can be repeated many times; the number of deposited layers is determined by the number of immersions of the support in water. This method for the preparation of monolayers and multilayers has been called the Langmuir–Blodgett method§.

Without considering in detail all the problems associated with DA monolayers and multilayers in view of the limited size of this review, we shall nevertheless mention a number of the most important studies. The synthesis and polymerisation of diynoic acids[257–266], the structure and morphology of the monolayers and multilayers formed[267–275], and their properties[276–280] have been described and their practical applications have been considered[190,252,253,281,282]. Naturally related problems have also been dealt with in some investigations.

Monolayers and multilayers which serve as models of biological membranes and are distinguished from other similar objects by improved properties have been created on the basis of diacetylenes. The syntheses and properties of compounds of this kind have been described[283–289].

The field of polymer and physical chemistry associated with the study of DA and polymers based on them is at present in a period of growth: the classes of newly synthesised DA are being expanded, the spectrum of their physical properties is increasing, new and interesting qualities of these materials have been discovered, and their practical applications have been extended. The studies which have been carried out are of interest also because the results obtained and the conclusions reached have a general bearing on all polymers with a conjugation system. The fact that many diacetylenes are obtained in the form of single crystals provides a unique possibility for their investigation by the latest experimental methods, many of which can be used also in the study of other polymers with conjugated bonds.

The investigations carried out have explained many hitherto obscure problems, for example, the influence of the system of conjugated bonds on the physical properties, the characteristics of the optical absorption and the role of excitons, the character and mechanism of the dark conductivity and photoconductivity, the problems of the initiation, mechanism and kinetics of polymerisation, and many others. Naturally there are also many unsolved problems in these fields. The study of the phase transitions in polydiacetylenes, which are accompanied by an alteration of many physical properties, is also of great interest. In this connection one must determine the order parameters and the critical parameters and compare the observed transitions with some kind of known model based on the theory of critical phenomena. Possibly one should also create an intrinsic theory.

The purely scientific interest and especially the prospects for the practical application of polydiacetylenes constitute an effective stimulus for their investigation and for general progress in this field.

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§ The First International Conference on Langmuir–Blodgett films whose Proceedings have been published in Thin Solid Films, 1983, **99**, Nos.1–3, has been held recently (Proceedings of the First International Conference on Langmuir–Blodgett Films, Durham, 1982). The history of the problem is described in the same volume; it contains methods for the preparation of films of this kind, particularly those based on DA, the methods for their investigation, the results of the latter, as well as a series of practical applications.

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Institute of Chemical Physics,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 178-199 (1984) U.D.C. 541.64

Some Problems of the Kinetics and Thermodynamics of Polymer Formation Reactions

V.V.Ivanov, M.A.Markevich, and V.I.Irzhak

The characteristic features of the thermodynamics, kinetics, and mechanism of the ionic polymerisation of oxygen- and nitrogen-containing heterocycles as well as aldehydes are considered. The interchain exchange and polymerisation reactions under non-standard physical conditions are discussed.
The bibliography includes 155 references.

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I. INTRODUCTION

Compared with anionic[1] and cationic[2] polymerisation of vinyl monomers, ionic processes involving the formation of heterochain polymers exhibit considerable specific features. Many fundamental characteristics of these processes have been observed in the study of the kinetics of the polymerisation of cyclic acetals and ethers, nitrogen-containing heterocycles, and aldehydes, which are largely examined below. In order to understand the complex kinetics of the ionic polymerisation of heterocycles, it is necessary to take into account the active role of the macromolecules formed, which influence all the steps in the polymerisation process—the initiation of the growing active centres and the propagation, transfer, and termination of the reaction chains[3].

One of the distinctive features of ionic polymerisation is the multiplicity of types of active centres (free ions, contact ion pairs linked to different extents, covalent centres, solvate-separated ion pairs, ion triplets, etc.), which exist in equilibrium, different active centres exhibiting different reactivities[1,4]. When the counterions are in addition linked to one another via the bond system of the polymer chain, a special type of ionic polymerisation arises—zwitterionic polymerisation characterised by specific kinetic and thermodynamic features.

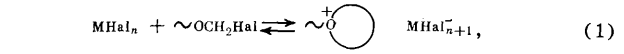
The thermodynamic parameters of polymerisation have been used traditionally to analyse the possibility of the conversion of a given monomer into a polymer. An important step towards the understanding of the general characteristics of polymerisation has been the determination of a relation between the kinetics and thermodynamics of heterophase polymerisation. The development of ideas concerning the dependence of the reactivity of the active centres on their phase state made it possible to explain the kinetics of the polymerisation reaction in which the polymer constitutes a separate phase.

This review deals with problems of the influence on the polymerisation kinetics of factors such as pressure, electric field, and other physical process conditions. The studies by N.S.Enikolopov included in the present review were completed mainly towards the 1970s, but they yielded many fundamental results which have exerted and continue to exert a significant influence on the development of the field under consideration.

II. CATIONIC POLYMERISATION OF HETEROCYCLES

Among the heterocyclic monomers polymerised via a cationic mechanism, cyclic acetals proved to be an extremely unusual class of monomers. The majority of the reactions in which acetals can participate are characteristic also of ethers, but the reactivity of the former is so much greater that the difference between them assumes a qualitative character. In particular, owing to the different reactivities of the acetal and ether linkages, the opening of the acetal ring in polymerisation takes place exclusively at the acetal linkage.

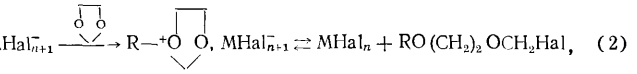
Accordingly, cyclic acetals should be much more reactive in polymerisation than, for example, tetrahydrofuran. In practice, the behaviour of cyclic acetals is much more complex: depending on the type of cationic catalyst, the rate of their polymerisation can be much greater than, similar to, or even lower than that of cyclic ethers. Tetrahydrofuran polymerises in the presence of different catalysts with similar process rate constants, while the effective rate constants for the polymerisation of 1,3-dioxolan in the presence of the same catalysts vary almost by four orders of magnitude[5]. The cause of this anomaly is associated with the influence of the nature of the counterion on the overall concentration of active centres: the following equilibrium plays the most important role in the establishment of the concentration of the active centres[5-12]:



(1)

where M is the metal (Sb, Sn, etc.) and Hal is the halogen. Other possible causes, namely the influence of the counterion on the state of the ions $\rightleftharpoons$ ion pairs equilibrium or the direct influence of the counterion on the reactivity of the active centres in the form of ion pairs, do not contribute significantly to the rate of reaction.

In many instances, an additional decrease in the concentration of the active centres associated with slow initiation is observed:



(2)

where R^+ is the cation of the initial salt.

Reactions (1) and (2) naturally do not exhaust all the different versions of the formation of active centres with reversible decomposition of the counterion; in the general case there is a possibility of a set of compounds of the type $MHal_{n-k}(^{\sim}OCH_2)_k$, where $k \leq n$, with the corresponding counterions $[MHal_{n-k+1}(^{\sim}OCH_2)_k]^-$. A spectroscopic confirmation of this fact has been described[13].

An important consequence of the decisive role of equilibria of type (1) is effective cocatalysis when substances which are ineffective as catalysts but can displace equilibrium (1) towards the active centres are introduced into the system (Table 1).

Table 1. The influence of the concentration of the added α-chloromethyl ether (c) on the rate (w) of the dissociation reactions of the acetal linkages*.[5,6,12]

Catalyst	$10^{-4}c$**, mole %	w/w_0***
Polymerisation of 1,3-dioxolan		
$(C_2H_5)_3O^+SbCl_6^-$	1.6	300
$SbCl_5$	0.7	190
$Ph_3C^+SbCl_6^-$	2.2	90
Methylal + ethylal model system		
$(C_2H_5)_3O^+SbCl_6^-$	7	25
$SnCl_4$	2	25

*Solvent—CH_2Cl_2; 20 °C.

**The concentration of the additive relative to the amount of the catalyst.

***Here w_0 is the rate of reaction in the absence of additives.

Thus in the case of cyclic acetals a type of "living" polymerisation obtains where only a small proportion of macromolecules grow in each instant but the dynamic equilibrium (1) ensures the possibility of the growth of all the chains throughout the process. In contrast to the usual polymerisation via the "living" chain mechanism, in the case of acetals, the concentration of the growing macromolecules is determined by the constant of equilibrium (1) and by the equilibrium constants of the analogous interactions of the initial and substituted Lewis acids with the polymer chain. On the basis of these ideas, it has been possible to explain the linear growth of the molecular weight of the polyacetals as a function of the degree of conversion, observed in many instances, i.e. a constant number of chains, which, however, is not identical to the number of catalyst molecules and depends on the temperature and other process parameters[14].

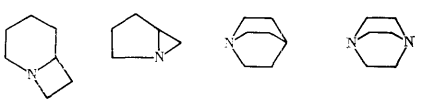
Later studies yielded convincing evidence showing that the equilibrium mechanism of the formation of ionic active centres plays an important role not only in the polymerisation of cyclic acetals but also in the cationic polymerisation of other heterocycles, particularly tetrahydrofuran[1,15-21].

The study of the polymerisation reactions of cyclic acetals permitted a significant step forward in the development of ideas concerning the relative reactivities of the free ions and ion pairs. The results of experiments designed to investigate the influence of the ionic strength of solutions and of the dielectric constant of the medium on the polymerisation process led to the conclusion that intense solvation of the cations by the monomers and delocalisation of the positive charge should equalise the reactivities of the free ions and ion pairs[22]. In contrast to the anionic polymerisation of vinyl monomers, the rate constants for the propagation of ions and ion pairs proved to be similar.

The initiation methods in the polymerisation of cyclic acetals are distinguished by a wide variety[4,5,23-33] in both the chemical and the kinetic sense. Depending on the reactivity of the active centres in relation to the acetal linkages and on the stability of the counterions, there is a possibility of the equilibrium[5,9,29,32], stationary[5], or mixed[5,10] initiation mechanisms. The case of the stationary mechanism, which obtains in the initiation of polymerisation by salts with fairly stable counterions, is extremely interesting; the initiation of the polymerisation of 1,3-dioxolan by the oxonium salt $(C_2H_5)_3O^+SbF_5^-$ can serve as an example of this kind[5].

The polymerisation of cyclic acetals is instructive also because many types of interactions characteristic of the cationic polymerisation of other heterocyclic monomers, for example, esters and ethers, are effectively realised in this process. The systems considered are characterised by a high sensitivity to the presence of microamounts of nucleophilic impurities (water, alcohols, etc.), the involvement in various stages of the reaction of not only the initial monomer but also of other heterocycles formed from the polymer chain via a depolymerisation mechanism, and the effective formation of complexes between different system components[34-46]. The proof of the fact that the polymer molecules are capable of participating, together with the monomer, in the formation of complexes with the catalyst and also in initiation, in reactions with the impurities, etc. was extremely important for the understanding of the experimental kinetics in the systems considered[34-36].

The cationic polymerisation of oxygen-containing heterocycles has much in common with the analogous processes involving many cyclic amines: 1-azabicyclo[4.2.0]octane (conidine), 1-azabicyclo[3.1.0]hexane (ABH), 1-azabicyclo[2.2.2]octane (quinuclidine), and 1,4-diazabicyclo.[2.2.2]octane (triethylenediamine):[47-49]



conidine ABH quinuclidine triethylenediamine

Table 2. The chain propagation rate constant (k_p) in the cationic polymerisation of conidine and the influence of catalysts of different types*.[47,48]

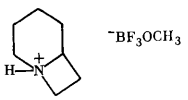
Catalyst	Concentration, M	k_p, litre mol^{-1} min^{-1}
BF_3-conidine	$5\cdot10^{-3}$	0.29
Ditto	$1\cdot10^{-2}$	0.48
Conidine hydrobromide	$5\cdot10^{-3}$	0.23
Ditto	$6\cdot10^{-2}$	0.38
N-Ethylconidinium iodide	$1\cdot10^{-2}$	0.21
Ditto	$6\cdot10^{-2}$	0.59

*Solvent—methanol; 60 °C.

The nature of the active centres for the polymerisation of cyclic amines is the same and is independent of the type of initiator: the active centres are quaternary ammonium salts. This is indicated, in particular, by the finding that the

chain propagation rate constant is independent of the nature of the initiator at the concentration of the active centres corresponding to their virtually complete dissociation into the free ions (see Table 2).

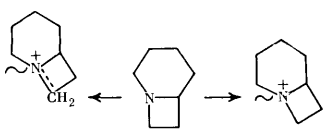
The structure of the initiating species in the conidine–CH_3OH–BF_3 system has been unambiguously established by ^1H, ^{11}B, and ^{19}F NMR.[49]



In virtually all cases the polymerisation of nitrogen-containing heterocycles is a process without termination, which proceeds via a mechanism of the "living" polymer type. In initiation by alkyl halides or quaternary ammonium salts, the rate of initiation is fairly high and the reaction takes place without an induction period and without self-acceleration. The molecular weight of the polymer increases in proportion to the initial monomer concentration and the degree of conversion and is independent of temperature, the monomer concentration, and the nature of the counterion. In the polymerisation of nitrogen-containing rings under the influence of acids, tertiary ammonium salts, and BF_3–monomer complexes, all the kinetic features fully agree with the mechanism involving a slow initiation stage. In conformity with this mechanism, the number-average degree of polymerisation $\bar{P}_n$ increases in proportion to the square root of the degree of conversion[5].

It is of interest to note the similarity between the nitrogen- and oxygen-containing rings in the sense that the tertiary ammonium ions used as catalysts react much more slowly with their monomers than R_4N^+, completely analogously to the mechanism of the inhibiting action of water in the polymerisation of oxygen-containing rings, where tertiary oxonium ions R_3O^+ are converted into the relatively inactive secondary ions R_2OH^+.

The available data show that the chain propagation in the polymerisation of cyclic amine proceeds via the nucleophilic attack on the active centre by the monomer; for example, in the case of conidine (the counterion is omitted) we have



The structure of the initial ring is retained in this process, while the reactivity is determined mainly by the ring strain[49].

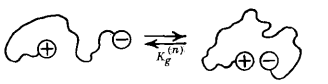
Conductimetric studies of ammonium salts in polymerising systems, experiments with added neutral salts, and the study of the influence of the nature of the counterion on the reaction kinetics suggest that the active centres in the polymerisation of nitrogen-containing rings are free ions and ion pairs[48]. The decisive argument in support of this conclusion is the change in the rate of polymerisation and the influence of neutral salts which suppress the dissociation of ion pairs and shift the equilibrium ions $\rightleftharpoons$ ion pairs towards the latter. In contrast to the majority of the data available at present, the rate of polymerisation increases in this instance, since ion pairs are more active than the free ions in the polymerisation of the cyclic amines investigated and the greater the size of the counterion the higher the rate constant for the propagation of the macroion pair. The size of the cation has an analogous influence on the process kinetics: the ratio of the rate constants for the propagation reactions involving the ion pair and the free ion is greater for a four-membered ring than for a three-membered ring in the presence of the same counterion.

The conclusion that the reactivities of the free ions and ion pairs in the polymerisation of cyclic amines are similar was confirmed later in studies by other workers[50]. A similar situation is typical for the cationic polymerisation of many other heterocycles, for example, tetrahydrofuran, oxepan, and sulphur-containing monomers[4,5].

III. ZWITTER-IONIC POLYMERISATION

In the ionic polymerisation of vinyl monomers and heterocycles, the mechanism by which the active centres formed by the ions are linked to one another solely by electrostatic interaction forces is most frequently encountered. However, there is a possibility of ways of initiating polymerisation in which dipolar active species (zwitter-ions) are formed and the subsequent growth of the polymer molecule takes place via the addition of the monomer molecules to the cation (cationic mechanism) or the anion (anionic mechanism); the anion and cation are then on the opposite ends of the polymer chain. The addition of monomer molecules does not alter the zwitter-ionic nature of the active centres and is accompanied by an increase of the number of covalent bonds between the oppositely charged groups.

A statistical description of the behaviour of the macromolecule in solution is based on the idea of a Gaussian coil, the average distance between the ends of which increases with increase of the chain length. In the case of a polymer zwitter-ion, the electrostatic interaction between the charges at the ends of the chain should lead to their mutual approach and the formation of an ion pair:



However, such a change in the coil conformation is accompanied by a decrease of the entropy of the macromolecule.

Allowance for the configurational statistics of the polymer chain and the law of electrostatic interaction between the charges of the polymer zwitter-ion made it possible to obtain an expression for the equilibrium constant of the dissociation of an isolated polymeric zwitter-ion as a function of the degree of polymerisation n:[52,53]

$$K_g^{(n)} = K_g^{(1)} n^{3/2},$$

where $K_g^{(1)}$ is a constant which depends solely on the thermodynamic flexibility of the chain. In contrast to the usual dissociation of electrolytes, including polymeric electrolytes, the dissociation constant of the growing zwitter-ion depends on its length and the probability of finding an active centre in the form of a free ion increases with increasing degree of polymerisation of the zwitter-ion. If the reactivities of the free ions and ion pairs are different and the former are more reactive, then the rate of growth of the polymeric zwitter-ion should increase with increase of its length. This fact, which is fundamentally new in polymer chemistry, seemingly contradicts Flory's fundamental postulate that the reactivity of the active centres is independent of the length of the macromolecule; however, in reality there is no contradiction here: the reactivities of the ion pairs and the free ions are independent of the length of the macromolecule and there is only a change in the probability of the existence of the active centres in these states.

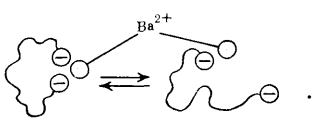
The anionic zwitter-ionic mechanism obtains in the polymerisation of acrylonitrile and its derivatives, β-propiolactone, and formaldehyde under the influence of triethylphosphine as the initiator and of ε-caprolactone and cyclic sultones under the influence of tertiary amines[54–67]; one of the examples of the cationic zwitter-ionic polymerisation is that of epoxides under the influence of BF_3.[68,69]

Another characteristic feature of the zwitter-ionic polymerisation initiated by triethylphosphine is the slow accumulation of ions in the system during the reaction which is due to the slow initiation. The increase of the overall concentration of ions owing to the initiator which has reacted leads to the suppression of the dissociation of the polymeric zwitter-ions via mechanism (3).† The decrease of the concentration of the free anions active in polymerisation also takes place owing to their interaction with the cations of the chains which have been destroyed. Since the ion pairs in the test systems are less reactive than the free ions, the suppression of polymerisation and even its complete arrest, unrelated to the exhaustion of the reactants, are observed during the process. The introduction of a fresh portion of the initiator does not then renew the polymerisation process.

The influence of these factors on the process kinetics has been analysed in relation to the anionic zwitter-ionic polymerisation of methacrylonitrile under the influence of $(C_2H_5)_3P$: the rate of polymerisation and the molecular weight of the polymer decrease during the process faster than would be expected solely from the decrease of the concentrations of the reactants[57,58].

An important kinetic consequence of the zwitter-ionic mechanism of polymerisation is the broadening of the molecular weight distribution (MWD) within the polymers with increase of the concentration of the monomer as a result of a sharp increase of the contribution of the free ions to the polymerisation with increase of the molecular weight of the growing polymer chain.

The ideas developed above concerning the specificity of the growth of the active centres in the form of zwitter-ions were extended subsequently to the anionic polymerisation of styrene under the influence of dianions combined with Ba^{2+} as the counterion: in this case the active centre dissociates only once in tetrahydrofuran:



Chain propagation takes place mainly with participation of singly dissociated barium salts of polystyrene which are in fact zwitter-ions: it has been established that the effective propagation rate constant increases with increased degree of polymerisation, in full agreement with one of the fundamental features of the kinetics of the zwitter-ionic polymerisation[53,70-73].

IV. THERMODYNAMICS OF POLYMERISATION

The relation between the rate of the process w_p and the equilibrium monomer concentration [A] is well known for homogeneous polymerisation:

$$w_p = -\frac{d[A]}{dt} = k_p c^* ([A] - [A]_{lim}) , \qquad (4)$$

where $[A]_{lim}$ is the limiting, equilibrium concentration of the monomer, c* the concentration of the active centres, and k_p the propagation rate constant. This law obtains in the polymerisation of many unsaturated and cyclic monomers for which the enthalpy and entropy contributions to the free energy of polymerisation are comparable in magnitude. However, another form of the relation between the process kinetics and thermodynamics, which obtains in those cases where the polymerisation is reversible but the polymer forms a separate phase, as, for example, in the heterophase polymerisation of trioxane, escaped the attention of investigators[74-85].

In a polymerisation system of this type the growing macromolecule can be either fully crystallised, so that the active centre is located on the surface of the polymer crystal, or is partly dissolved in the reaction medium, whereupon the active centre is located at the end of the dissolved section of the polymer chain. The equilibrium monomer concentrations in relation to the polymer in the dissolved and crystalline states are different. The addition of the monomer to the surface active centre with formation of a solid polymer is thermodynamically more favourable, so that the equilibrium monomer concentration is in this case lower than in relation to the polymeric centre in solution.

Thus processes involving the addition of the monomer to the active centre at the dissolved end fragment of the macromolecule, the reverse reaction involving the depolymerisation of this section of the chain, chain propagation, the depolymerisation of the active centres on the surface of the crystal, as well as the crystallisation and dissolution of the growing chain takes place in the polymerisation system. The character of the dependence of the rate of reaction on the monomer concentration is determined by the ratios of all these processes. If, for example, the rate of crystallisation is lower than the rate of growth of the dissolved part of the macromolecule, then chain propagation takes place mainly at the active centres in solution and the process is described by the equation for reversible polymerisation [Eqn.(4)] with $[A]_{lim}$ corresponding to the monomer $\rightleftharpoons$ dissolved polymer equilibrium.

With decrease of the monomer concentration, the rate of growth of the dissolved part of the macromolecule becomes less than the rate of crystallisation and the kinetics are described by the same equation (4) but with another limiting monomer concentration, that in equilibrium with the crystalline polymer.

Accordingly, a number of anomalous features are observed in the polymerisation of trioxane: apparently high reaction orders with respect to the monomer and their dependence on the nature of the solvent, temperature, etc. These features cannot be explained by any ideas concerning the ionic liquid-phase processes other than those described above.

The situation where not only the initial monomer but also other "secondary" comonomers, formed via a depolymerisation mechanism, are in equilibrium with the polymer chain is fairly common. The study of a system of such equilibrium yields valuable additional information about the process. In the polymerisation of trioxane not only the initial monomer (Tr) but also formaldehyde (F) and an eight-membered cyclic acetal–tetraoxane (TTR) (larger rings are present in smaller amounts) are present in the system in equilibrium with the polymer, so that the process can be described by the following scheme:

$$\begin{array}{c} F \\ \downarrow\uparrow \\ T_r \rightleftarrows P_d^{(\nu)} \rightleftarrows P_s , \\ \uparrow\downarrow \\ TTR \end{array}$$

where P_s and $P_d^{(\nu)}$ are the solid polymer and the dissolved ends of the polymer chain with a degree of polymerisation ν respectively. This scheme makes it possible to explain the dependence of the stationary formaldehyde and tetraoxane concentrations on that of trioxane and also the anomalous dependence of the rate of polymerisation and of the induction period on the initial monomer concentration[81].

†Mechanism (3) is not shown in the original Russian text (Ed.of Translation).

Another important aspect of the kinetic-thermodynamic approach to polymerisation processes is the possibility of regulating the polymer structure by carrying out the reaction in the vicinity of the thermodynamic monomer–polymer equilibrium. The essential feature of such regulation consists in the following. The differences between the chemical potentials of the states of the polymers having different structures at high monomer concentrations, i.e. under conditions remote from equilibrium, are usually significantly smaller than the change in the chemical potential in the monomer–polymer transition. Therefore, all possible structures of the polymer are thermodynamically almost equally probable and the preferential selection of structures takes place only for kinetic reasons as a function of the type of catalyst, temperature, and solvent. However, if the polymerisation is carried out under conditions close to the monomer–polymer equilibrium, then certain structures are thermodynamically prohibited, so that at low monomer concentrations small differences between the chemical potentials of the initial and final states of the polymer can be both positive and negative. In the limiting case, the polymer formed must have only the thermodynamically most favourable structure.

If one considers the supermolecular structure of the polymer, it is found that the latter varies with the ratios of the rates of three processes: the chemical formation reaction of the polymer, the segregation of the polymer as a separate phase, and structural transformations within the polymer phase. Different supermolecular structures have indeed been observed in the polymerisation of a series of monomers in different solvents with variation of the thermodynamic polymerisation conditions by varying the monomer concentration. For example, in the polymerisation of trioxane and triethylenediamine, small globular structures are formed at a high monomer concentration, while at low concentrations the products are large well-organised lamellar crystals[86–88].

V. SOLID-PHASE POLYMERISATION

The kinetics of reactions in the solid phase are significantly specific. The differences between them and those of reactions in the gas and liquid phases are related, on the one hand, to the difference between the energies of individual molecules and the appearance of collective energy levels and, on the other, to the geometrical fixation of the molecules in space relative to one another and the appearance of different types of defects in the structure of the substance.

The study of solid phase polymerisation developed extensively in the 1960s and has at present become an independent branch of polymer chemistry. The polymers formed in the solid phase differ in their chemical structure, stereoregularity, crystallinity, and orientation from the polymers synthesised by the usual methods in solutions[89]. Studies of the polymerisation of various monomers (trioxane, tetraoxane, hexamethylcyclotrisiloxane, etc.) in the solid phase under the influence of ionising radiation or ionic catalysts established[90] that the polymerisation kinetics are in many respects identical regardless of the method of initiation. This made it possible to devise a general kinetic scheme for solid phase polymerisation taking into account the characteristic features of the structure of the solid. This concept is based on the following ideas[90].

1. As a result of the virtually complete absence of the translational diffusion of polymer molecules, monomer molecules, or various impurities, the migration of the active centre in space and its collisions with the monomer or impurities take place mainly as a result of chain propagation steps.

2. The inhomogeneities in the crystal lattice (dislocations, tracks, vacancies, etc.) are the sites where the growing polymer chains are terminated.

3. The anisotropy of the reactivity of the macromolecules growing in the crystal lattice determines their preferential growth along one of the crystallographic axes.

Thus the active centres having the same chemical structure but located in different environments exhibit different reactivities. The transfer of the active centre from one environment to another takes place as a result of the chain propagation step or some kind of physical process involving a change in the structure or in the perfection of the crystal lattice[90–94].

VI. POLYMERISATION UNDER EXTREME CONDITIONS

Together with the traditional chemical methods for influencing ionic polymerisation processes, considerable possibilities are associated with physical methods. Only the influence of the temperature and medium are widely used in practice; the influence of a high pressure and an electric field have been much less investigated but are extremely promising.

1. Polymerisation Under Pressure

Although the form of the dependence of the rate constant for an elementary reaction k on the pressure p is general and is described by the formula

$$\frac{d \lg k}{dp} = -\frac{\Delta V^{\neq}}{RT},$$

where $\Delta V^{\neq}$ is the change in volume on activation, the influence of pressure on polymerisation can be extremely complex because different values of $\Delta V^{\neq}$ occur for different elementary polymerisation steps. This has been established in a comparative study of the influence of pressure on the radical polymerisation of propene and methyl methacrylate, the cationic polymerisation of styrene and tetrahydrofuran, and the solid-phase polymerisation of trioxane[95,96].

In the radical polymerisation of α-olefins the possibility of obtaining a high-molecular-weight polymer is limited by the appearance in the chain propagation reactions of the relatively inactive allyl radicals, formed as a result of chain transfer to the monomer. It has been shown[95] that the application of pressure (>3000 atm) in the polymerisation of propene imparts "life" to the allyl radicals with a significant increase of the reinitiation rate constant. The influence of pressure on the molecular weight obeys a complex relation; however the growth of $\bar{P}_n$ with pressure is highly pronounced. In the radical polymerisation of methyl methacrylate, an increase of pressure leads to an increase of both the rate of polymerisation and of the molecular weight, which is related to the increase of k_p and the decrease of the rate constant for the destruction reaction.

In the cationic polymerisation of styrene under the influence of $HClO_4$ in chlorobenzene, a significantly more appreciable accelerating influence of pressure is observed than in radical polymerisation; this difference has found a natural explanation as a result of the decrease of the dielectric constant under the influence of pressure[96].

The solid phase polymerisation of trioxane (in the presence of I_2 as the initiator at 50–70 °C) is sharply retarded with increase of pressure, which is accompanied by the anomalously high value $\Delta V^{\neq} = 120$ cm^3 mol^{-1}. In this process the polymer chain is known to grow while disrupting the crystal lattice of the monomer[90]; pressure prevents such breakdown and leads to an effective decrease of the rate of polymerisation.

Unexpected effects were obtained when a system undergoing polymerisation was subjected to the simultaneous influence of pressure and shear deformations (see Zharov's review in the present issue).

2. The Influence of the Electric Field

Ionic polymerisation systems are in essence aqueous solutions of electrolytes in which some of the ions are active centres in the growing polymer chains, i.e. are fixed on macromolecules. By applying an electric field, it is possible to displace the ion pairs $\rightleftharpoons$ free ions equilibrium towards the latter in a manner very familiar for many of the usual systems in high electric fields whose strength exceeds 50 kV cm^{-1}.

In contrast to low-molecular-weight electrolytes, the mobility of the macroion is significantly lower than that of the counterion. As a consequence of this, the application of an electric field entails the formation of a space charge in fields whose strength is ~1 kV cm^{-1} together with an increase of the degree of dissociation of the polymeric ion pairs (as a result of the preferential removal of the counterion to the electrode). A detailed theory of the transient processes occurring in polymerisation systems following the application of an external field has been developed[97–99] and a relation has been established between the parameters of the electric field and the reaction kinetics.

When both macrocations and macroion pairs with propagation rate constants k_+ and $k_\pm$ are involved in the process simultaneously, the corresponding ratio of the rate of polymerisation in the electric field (w_E) to that in its absence (w_0) is

$$\frac{w_E}{w_0} = \frac{1 + (k_\pm/k_+ - 1)\,\bar{P}_E/c_0}{1 + (k_\pm/k_+)\,\alpha} ,$$

where c_0 is the concentration of the active centres, α the degree of their dissociation, and $\bar{P}_E$ the average stationary concentration of active centres, which depends on the mobilities of the macroion and counterion, the electric field strength, and the rate constant for the discharge of the ions at the electrode. The conditions under which the rate of polymerisation should increase or the latter should be inhibited following the application of a field have been determined[97,98,100]. Together with the change in the rate of polymerisation under the influence of the electric field, the molecular weight of the polymer increases. For a specific ratio of the constants $k_\pm$ and k_+, the degree of polymerisation increases throughout the reaction volume or in separate sections of the latter[101,102]. For example, the rate of polymerisation of trioxane under the influence of $SnCl_4$ in nitrobenzene increases by a factor of 2–7 when a field is applied, while the molecular weight of the polymer doubles[102].

3. Polymerisation Near the Consolute Point

One of the first studies of polymerisation near the consolute point for a binary liquid mixture was that of the radical polymerisation of acrylonitrile in heptane in the region of the phase diagram which includes the consolute point and corresponds to the separation of the system into two phases[103]. The interest in these investigations is due to the fact that, in the vicinity of the consolute point, there is an anomalous decrease of the macroscopic diffusion coefficient, an enhancement of the concentration fluctuations, an increase of the viscosity of the system, etc. It is to be expected that the anomaly in the physical properties of the medium has an unusual effect on the polymerisation reaction. Indeed, in the polymerisation of acrylontrile in the vicinity of the consolute point, distinct minima are observed in both the rate of polymerisation and in the molecular weight of the polymer. Kinetic studies combined with the investigation of the state of the system near the consolute point by the paramagnetic label method suggest that the polymeric radicals can give rise to stable clusters[103–105]. Similar phenomena apparently play a significant role in certain multiphase systems.

VII. INTERCHAIN EXCHANGE IN POLYMERS

In 1962 Enikolopov[106] pointed out the possibility of interchain exchange in polymerisation reactions and proposed a mechanism for this reaction, which was subsequently called the reaction involving chain transfer via the polymer with the dissociation of the macromolecule (CTD).[107–110]

The interchain exchange reactions in polycondensation processes had been well known long before the studies of Flory and Korshak were undertaken[111–114]. However, it was believed that interchain exchange is possible only in polycondensation processes and it was regarded as one of the fundamental differences between polycondensation and polymerisation processes. It is nowadays generally recognised that the capacity for interchain exchange is determined solely by the structure of the macromolecule and the type of the active centre and is characteristic of all heterochain polymers regardless of the method of their synthesis.

The essential feature of the CTD reaction is the exchange interaction of two chains, one of which constitutes the active centre and the other an inactive macromolecule, which proceed via a heterolytic or homolytic substitution mechanism. In a general form, the mechanism of the CTD reaction can be represented schematically as follows:

$$\sim(R^1)^{\bullet} + \underset{\displaystyle R^3}{\overset{\displaystyle R^2}{X}} \rightleftarrows \sim R^1\!-\!\underset{\displaystyle R^3}{\overset{\displaystyle R^2}{X^{\bullet}}}\!- \begin{cases} \rightleftarrows \sim(R^2)^{\bullet} + \sim R^1XR^3\sim \\ \rightleftarrows \sim(R^3)^{\bullet} + \sim R^1XR^2\sim \end{cases} \qquad (5)$$

where X is a heteroatom (O, N, S, P, Si, etc.) and $\sim(R^i)^*$ an active macrospecies (cation, anion, or radical).

The above mechanism is fairly universal and makes it possible to understand the fundamental kinetic features of the ionic polymerisation reactions of heterocycles and also the form of the variation of the molecular weight distribution of the macromolecules in these processes.

The CTD reaction is in essence yet another stage (together with chain initiation, propagation, and transfer reactions) in the formation reactions of macromolecules.

1. The CTD Reaction as a Factor Governing the Attainment of the Equilibrium Distribution of Macromolecules

It is seen from Scheme (5) that a process occurring via the mechanism indicated is reversible and should lead to a redistribution of the macromolecules with respect to size and composition, i.e. should influence important properties of the

polymers formed, such as the MWD and the distribution of units in the copolymers, which determine in their turn the fundamental physicomechanical and rheological characteristics of the polymers. Evidently[74,115,116] an equilibrium characterised by the most probable distribution of macromolecules with respect to size must be ultimately established in the system where the CTD reaction takes place; here one must note particularly that this distribution is established regardless of the details of the mechanism and the rates of any other reactions occurring in the system. For linear molecules, the equilibrium MWD function is

$$\frac{[R_j]}{\sum_{i=1} [R_i]} = \frac{1}{P_n} \exp(-j/P_n), \qquad (6)$$

where $[R_j]$ is the concentration of macromolecules with a length j and P_n is the number-average degree of polymerisation.

It is noteworthy that the above MWD function is used only for the description of macromolecules with flexible chains; for macromolecules with rigid chains, the MWD function becomes narrower and, for example, for rigid rods, assumes the form[107,117]

$$[R_j] \propto j^2 \exp(-3j/P_n).$$

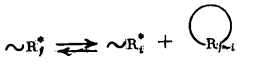
The form of the equilibrium distribution function is also determined by the interaction of the macromolecules with the medium: in a θ-solvent, in moderately concentrated solutions, and in bulk, Eqn.(6) is valid, while in the case of a dilute solution in a good solvent the exponential distribution assumes a different form[110,116]:

$$[R_j] \propto \exp\left(\frac{5}{2}\alpha^2 + \ln \alpha^3 - \gamma j\right),$$

where γ is a constant coefficient and α the degree of swelling of the macromolecule in solution, which depends on its length (i.e. on j).

If the polycondensation or polymerisation reaction takes place in a poor solvent, from which the polymer is precipitated to form a separate phase, then the equilibrium MWD is also exponential. A detailed thermodynamic analysis of such systems has been carried out[116].

It follows from Scheme (5) that the object of attack by the active centre of the macromolecule can also be its own chain. Evidently, under these conditions cyclic macromolecules with different molecular weights are formed together with linear macromolecules. This situation is fairly characteristic and in many polycondensation (the formation of polysiloxanes, polyesters, polyamides, etc.) and polymerisation (the synthesis of polyacetals, polyesters, polyethers, polyamides, etc.) processes the formation of both low- and high-molecular-weight cyclic products is observed[107,110-113]. In this case the CTD reaction can be represented schematically as follows:



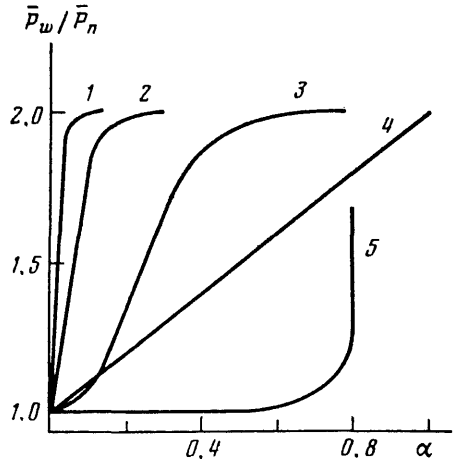
Apart from monocyclic species, in concentrated solutions of polymers with flexible chains there is a possibility of the formation of catenanes and in the case of polyfunctional polymers rings with a very complex topology can be produced[118] (pp.133–139).

The equilibrium distribution of rings with respect to size has been obtained on the freely jointed chain model[119]:

$$[R_j] \sim j^{-5/2} \exp(-j/P_n). \qquad (7)$$

This equation is valid only for the description of MWD of fairly large rings; on the other hand, in the case of small and moderately large rings (up to 10–12 members) their energy strain plays an important role and Eqn.(7) therefore becomes unsuitable.

We considered above the MWD functions at equilibrium, which can be established in a macromolecular system not only via the mechanism of a CTD reaction but also as a result of polycondensation or reversible polymerisation. The fundamental difference between these mechanisms of the formation of a polymer with an equilibrium MWD consists in the kinetics of its attainment[107,120-123], which is illustrated in the Figure. In polycondensation, the parameter $\bar{P}_w/\bar{P}_n$, characterising the width of the distribution, increases linearly with the degree of conversion (see Figure, curve 4). In reversible polymerisation a narrow MWD ($\bar{P}_w/\bar{P}_n = 1$) is maintained virtually until the attainment of the equilibrium degree of conversion and $\bar{P}_w/\bar{P}_n \to 2$ only within a very short range of degrees of conversion following the attainment of equilibrium (curve 5). In contrast to the previous instances, the rate of establishment of the equilibrium MWD in a CTD reaction depends on the chain length and increases sharply with increase of the latter (curves 1–3) owing to the increase of the number of reaction centres.



The character of the variation of the width of the distribution ($\bar{P}_w/\bar{P}_n$) in polymerisation and polycondensation processes[107]: 1)–3) polymerisation without chain termination and with instantaneous initiation in the presence of CTD [$k_{CTD}/k_p = 1$; monomer/catalyst concentration ratio: 1) 10^4; 2) 10^3; 3) 10^2]; 4) linear polycondensation in the absence of CTD; 5) reversible polymerisation without chain termination and chain transfer; α = degree of conversion.

The results of the analysis of the kinetics of the attainment of the equilibrium MWD, presented in a general form in the Figure, show that the CTD reaction is a much more vigorous process, leading to the attainment of the equilibrium MWD, than polycondensation or reversible polymerisation. The character of the $\bar{P}_w/\bar{P}_n$–α kinetic curves is a criterion of the occurrence of the CTD reaction in the reaction system and is used for a quantitative assessment of the relative rate of this reaction ($\varepsilon = k_{CTD}/k_p$, where k_{CTD} is the rate constant for the CTD reaction and k_p the chain propagation rate constant). In particular, such estimates have been carried out for polyacetals[122] and polyethers[123].

When copolymer formation reactions are considered, the question of the kinetics of the attainment not only of the equilibrium MWD but also of the equilibrium distribution of the macromolecules with respect to composition and of the distribution of units in the chain arises.

It has been shown theoretically that the distribution of the sequences of units of each type with respect to length in the copolymer obeys an exponential law[107] and the average number of blocks in the chain (l) is described by the expression[124]

$$l^2 = K(m_a - l)(m_b - l) ,$$

where K is a combination of the rate constants for the cross-exchange reactions between the chains, l the number of blocks of units of a given type in the chain, and m_a and m_b are the total numbers of monomeric units of types A and B respectively.

The relations obtained have been confirmed experimentally for a series of objects in a number of investigations[11,36,40,46,125–131]. It is noteworthy that in the general case the quantitative study of the formation of polymers in the interaction of two homopolymers or the study of the polymerisation of one of the monomers in the presence of another homopolymer is extremely difficult and this problem has been solved successfully only in the study of thermostable formaldehyde copolymers[127,129]. However, the problem simplifies considerably if one employs model low-molecular-weight compounds. In this case it is possible not only to estimate the combinations of the constants for the cross-exchange between the chains but also to determine separately all the rate constants for the elementary reactions[11,126,128,131].

2. The Role of CTD in Individual Stages of the Polymerisation Process

A second important aspect arising when the formation reactions of heterochain polymers are considered is the need to allow for the active role played by the resulting macromolecules themselves. Indeed, it is seen from Scheme 5 that the CTD reaction proceeds via an intermediate stage involving the formation of an unstrained 'onium ion whose reactivity differs in the general case from that of the growing active centre. As a consequence of this, the nature and concentration of the active centres change. The kinetic effects are then in essence caused by the competition between the chain propagation reactions at the free active centres (R_j^*) and the active centres bound in a complex with a macromolecule (R_jp)*. These reactions can be represented by the following kinetic scheme:

$$R_j^* + m \xrightarrow{k_1} R_{j+1}^* ,$$

$$R_j^* + p \rightleftarrows (R_jp)^* ,$$

$$(R_jp)^* + m \xrightarrow{k_2} R_{j+1}^* + p .$$

Evidently, the case where $k_2 < k_1$ corresponds to the progressive retardation of the chain propagation reaction. If $k_2 = 0$ and the equilibrium in the complex formation reaction between the growing active centre and the macromolecule is strongly displaced to the right, the implication is that the growing active centres are deactivated in the given system and that the rate of polymerisation decreases until the complete arrest of the reaction. It has been shown in a series of experimental studies that both these cases are characteristic of the ionic polymerisation of heterocycles[14,22,35,132,133]. Thus in the cases considered, the influence of the macromolecules formed reduces mainly to the inhibition of the polymerisation process.

The macromolecules are actively involved also in the initiation stage[107], because the growing active centres can be formed in the interaction of the catalyst (Ct) with both the monomer and the polymer:

$$Ct + m \xrightarrow{k_1} R_1^* ,$$

$$Ct + p_j \xrightarrow{k_2} R_i^* + p_{j-i} .$$

Under the influence of the catalyst, the macromolecules decompose under these conditions to yield growing active centres, which do not differ in their chemical nature from those arising on direct interaction of the catalyst with the monomer. When $k_2 > k_1$, the rate of accumulation of the active centres in the polymerisation system increases progressively, so that the polymerisation should be clearly autocatalytic. A whole series of similar instances have been observed experimentally in the cationic polymerisation of cyclic acetals under the influence of protic and aprotic acids[29,36,134].

The second possible version of the involvement of macromolecules in the initiation step corresponds to the scheme

$$Ct + m \xrightarrow{k_1} R_1^* ,$$

$$Ct + p_j \rightleftarrows Ct p_j .$$

In this case, the macromolecule reacts with the catalyst molecules to form complexes which are inactive in polymerisation, playing the role of a kind of inhibitor. The fraction of the catalyst bound in a complex with the polymer is determined by the relative basicities of the heteroatom in the monomer and polymer molecules. Such a situation frequently arises in the polymerisation of many cyclic ethers under the influence of Lewis acids[135,136].

If a low-molecular-weight substance is present in the polymerisation system and is involved in the reaction as a chain transfer agent, then the reaction

$$R_j^* + XY \xrightarrow{k_n} R_jY + X^*$$

results in the formation of an active fragment X* whose reactivity towards the monomer is in general different from that of the growing active centre. The reinitiation reaction can occur when the active fragment X* interacts with the monomer or polymer molecule:

$$X^* + m \xrightarrow{k_1} R_1^* ,$$

$$X^* + p_j \xrightarrow{k_2} R_i^* + p_{j-i} .$$

If the case where $k_1 \ll k_p$ and $k_2 \gg k_1$ obtains, then analysis shows[107] that a completely unusual autocatalytic character of the polymerisation process itself and the consumption of the chain transfer agent should be observed. Such a case has in fact been noted in the polymerisation of dioxolan in the presence of chain transfer agents generating a proton as the active fragment[137].

The different versions examined demonstrate convincingly that one cannot understand the extremely complex kinetics of the ionic polymerisation of heterocycles without taking into account the active role which the macromolecules formed themselves play in such polymerisation. The macromolecules influence all the stages of the polymerisation process—the initiation of the growing centres and the propagation, transfer, and termination of the reaction chains. This influence is exerted because each active species in the system is capable of reacting with any unit of the polymer chain to form an active centre bound in a complex, whose decomposition results in the formation of new active centres with a modified reactivity.

This is manifested particularly strikingly in the copolymerisation of heterocycles when the interchain exchange processes occurring in the system supplement the cross-exchange reactions, which leads to an alteration of the concentrations of all types of growing active centres. In consequence of this, the dependence of the composition of the copolymer formed on that of the monomer mixture is not described by the classical Mayo-Lewis equation. This problem has been analysed in detail and methods have been developed for the determination of the copolymerisation constants in the presence of the CTD reaction[107,126]. The use of the classical version of the Mayo–Lewis equation leads to effective copolymerisation constants which must be approached with much caution.

It remains to note yet another important feature of systems in which the CTD reaction occurs, namely the appearance of a special kind of "living" state of the polymerisation system[107, 109,114,138]. It is characterised by the fact that, in contrast to the classical "living" polymerisation[1], in the CTD reaction each "dead" macromolecule can be "revived" regardless of the nature of the terminal groups. This ultimately results in the involvement of all the macromolecules, both "living" and "dead", in the propagation process.

One of the important aspects of the relevant studies is investigation of the detailed mechanism of the elementary step in the CTD reaction. In a general form, it can be represented by Scheme (5), but in each specific instance, when the chemical nature of the polymer chain is varied, the actual reaction mechanism becomes more complex. Nevertheless, in all the instances investigated, it has been shown that the reaction must proceed via the intermediate formation of an active growing centre bound in a complex with a macromolecule[40,107,120,132]. For example, it has been shown[132] that the interaction of the macrocation with the chain leads to a large increase of viscosity owing to the effective increase of the molecular weight.

The exchange reactions can be simply and conveniently modelled with the aid of low-molecular-weight compounds, which simulate particular functional groups involved in the CTD. The low-molecular-weight compounds model either the reagent (the growing active centre) and the substrate (the macromolecule attacked by the active centre) or only the substrate. In the latter case only the chain transfer to the low-molecular-weight compound is in essence investigated. Such studies have been carried out for a whole series of compounds: ethers[120], esters[40,46,125,139–142], and acetals[4,11, 36,106,143]. The available information about the mechanisms of many interchain exchange reactions in various derivatives of carboxylic acids, sulphur-, phosphorus-, silicon-, and metal-containing compounds, and certain other systems has been surveyed and described systematically in a monograph[107].

3. CTD As a Method of Synthesis

The possibility of the practical employment of interchain exchange reactions for the synthesis and chemical modification of polymeric materials is very important. Their use for the synthesis of statistical block and graft copolymers as well as polymers with specified terminal functional groups is most promising. In principle, there is a possibility of two methods of synthesis of copolymers using interchain exchange reactions: the polymerisation of the monomer in the presence of another homopolymer and the interaction of two homopolymers.

In the former case, i.e. in the polymerisation of the monomer in the presence of another homopolymer, the polymerisation is accompanied by CTD to the "foreign" homopolymer present in the system. At the beginning of the process, a block copolymer is formed and then transformed into a statistical copolymer as the vigorous interchain exchange reaction proceeds. This method has been applied to a number of systems, in particular to the cationic polymerisation of cyclic ethers, esters, and acetals in the presence of heterochain polymers of different kinds[130,133,144].

If the comonomers differ sharply in their reactivities, then their copolymerisation leads initially to the homopolymerisation of the more reactive monomer and then the less reactive monomer polymerises in the presence of the second homopolymer. In the absence of interchain exchange such a reaction would have led to the formation of a mixture of homopolymers but in systems where a sufficiently intense interchain exchange takes place a statistical copolymer is produced. The copolymerisation of trioxane with dioxolan, where the latter is consumed during the induction period of the polymerisation of trioxane, proceeds in this particular way[145]. A similar situation obtains also in a number of other systems[107].

In such cases one should speak of polymerisation in the presence of another homopolymer rather than copolymerisation, although externally the process appears to be the usual copolymerisation. On this basis, a method has been developed for the synthesis of mixed carboheterochain block copolymers[146], which is the most general of those known at the present time[107]. It consists in the cationic or anionic polymerisation of vinyl monomers in the presence of heterochain polymers, whose bonds may be ruptured under the influence of the growing ions. This method is entirely universal; any heterochain polymers obtained by both polymerisation and polycondensation can be used in the reactions and the reaction itself can be carried out both homogeneously and heterogeneously. It is important that the polymerisation process can also be carried out directly on the finished articles (fibres, films) made of heterochain polymers, which makes it possible to modify the properties of only a thin surface layer.

When two homopolymers interact in the presence of a catalyst, block or statistical copolymers are also produced[107].

If the heterochain homopolymer is made to react with low-molecular-weight compounds, which behave as agents transferring the reaction chain, then the polymer is degraded and the chains formed contain the corresponding terminal groups. This principle has been used to obtain polymers and oligomers with specified end groups and it can be applied also in the usual version of the polymerisation of a monomer in the presence of a chain-transfer agent[107]. When the interchain exchange reactions take place in such systems, the relative rates of consumption of the reactants (of the monomer and the chain-transfer agent) are unimportant for the final result, since a continuous redistribution of the end groups in the macromolecule takes place under these conditions.

The above methods for the modification of heterochain polymers have been used successfully for the solution of various practical problems and in the first place for the thermal stabilisation of polymers based on formaldehyde. Above the limiting temperature, such polymers decompose fully to the monomer as a result of depolymerisation. This virtually precludes their conversion into finished articles, since the temperature at which this is done usually exceeds the limiting temperature. This contradiction can be resolved by creating conditions under which the induction period of the given chain process is significantly longer than the time necessary for the working of the polymer. Depending on the degradation mechanism[110], this can be achieved in two ways. If the initiation reaction of the thermal degradation of the polymers begins from the end of the chain, then end groups whose thermal decomposition takes place above the limiting temperature for the given polymer must be introduced

into the latter. On the other hand, if the initiation is random, as, for example, in the thermo-oxidative degradation of polyformaldehyde, then the introduction of stable units by the formation of a copolymer makes the kinetic chain length in the degradation process significantly smaller than the average chain length of the copolymer.

Both these procedures have been applied successfully using the interchain exchange reaction for the solution of the problem of the thermal stabilisation of polymers based on formaldehyde. The following methods have been developed for the synthesis of formaldehyde homopolymers and block copolymers via a cationic mechanism (using catalysts of the type of Lewis acids and their complexes): (a) polymerisation with stabilisation of the end groups via chain transfer to low-molecular-weight linear acetals[147,148]; (b) copolymerisation of formaldehyde with cyclic acetals[149, 150]; (c) polymerisation of formaldehyde accompanied by chain transfer with dissociation of macromolecules into polymeric acetals or ethers[127,151,152]; (d) exchange reactions between polyformaldehyde and linear polyethers and polyacetals[153].

The study of copolymerisation by the second of the methods listed above in the gas phase in a flow system showed that a special type of copolymerisation takes place in which a true copolymer is obtained despite the fact that the monomers are polymerised on active centres of different types[149].

Oligomeric products of different types with two functional reactive groups, obtained using the interchain exchange reaction, found extensive applications as starting materials for the synthesis of polymers, plasticisers, intermediates in organic synthesis, surfactants, etc.[107,120,154]

One of the exceptionally important problems in practice is the employment as a secondary starting material of used articles made of polymeric materials or of industrial waste. In the case of polymers having heterocarbon linkages in the main or side chains, the application of the interchain exchange reactions to the solution of this problem is of interest. A series of successful examples of this kind already exist[107,155], but the extensive possibilities inherent in the interchain exchange reaction for such purposes have still been inadequately employed in theoretical research and in practice.

This review has dealt with the results of kinetic and structural studies of cationic polymerisation reactions of heterocycles. The set of data obtained for the mechanisms of the reactions investigated demonstrate convincingly the fruitfulness of the kinetic approach. Further development of this field will be directed towards the determination of quantitative kinetic data; this will make it possible to develop and supplement the existing ideas concerning the nature of the active centre in the cationic polymerisation of heterocycles and to establish a relation between its reactivity and structure.

An important kinetic method involves the study of low-molecular-weight models. In this case it is frequently possible to obtain the most clear-cut correlations between the kinetic constants and thermodynamic parameters, i.e. the structure of the reacting substances. However, the complete transfer of the results obtained to polymeric objects is not always possible, since the polymeric nature and the specific features of the physical state of the polymer chain are in many instances largely manifested in the chemical reactions of the polymers; an example of this is provided by zwitter-ions. Allowance for the physical state of the system in the study of the kinetics of the formation reactions and transformations of macromolecules becomes more important the finer the details of the mechanism in which the investigator is interested.

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Institute of Chemical Physics,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 200-222 (1984) U.D.C. 678.742;541-64:547.31

The Synthesis and Properties of Polymerisation-filled Polyalkenes

F.S.D'yachkovskii and L.A.Novokshonova

The general principles of the polymerisation filling of polyalkenes and various other polymers have been examined. Physical and chemical methods for activating mineral and organic fillers, which lead to the production on their surface of active centres initiating polymerisation processes, have been discussed. The kinetic characteristics of the polymerisation of various monomers on a surface have been examined. The results of studies of the properties and various characteristic features of the structure of polymerisation-filled compositions have been described.
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I. INTRODUCTION

The importance of filled polymers has increased sharply in recent years. This is due to two factors: firstly, the introduction of mineral and organic fillers into polymers gives materials with a new set of properties, and secondly, the presence of fillers leads to a decrease in the relative proportion of polymer in the final product, giving a saving in organic raw material or an increase in the production of the final product for the same amount of polymer. The rate of increase in the production of fillers for polymers in the developed capitalist countries is several times the rate of development of the production of polymeric materials[1-3]. Among the plastics produced at present, the greatest tonnage corresponds to polyalkenes (polyethylene, polypropylene), polyvinyl chloride, and polystyrene plastics. Thus the development of effective methods for introducing fillers into these polymers to obtain constructional materials for various purposes based on them is a task of practical importance.

The traditional method of obtaining filled thermoplastics involves the mechanical mixing of the polymer and the filler in powdered form or the combination of the components in a polymer melt. At the present time, practically all forms of filler in other countries are treated with special substances, or finishes, such as silanes and titanates[2], which give the surface of the filler improved adhesive properties with respect to the polymer. The aim of the finishing is to increase the degree of filling, and to improve the physicomechanical properties of the composites and their workability. The finishing of fillers is a multi-stage energy-consuming process. The expenditure on the preparation of the mixture compositions is 20-30% of the cost of the composite[3].

In spite of all the difficulty of introducing a filler into a polymer, considerable progress has been made in this field, and the world production of filled compositions is increasing steadily[1-3]. In 1975, a fundamentally new way of obtaining filled polymers was proposed, namely polymerisation filling, in which the polymer-filler composition is obtained by polymerising the corresponding monomer on the surface of an organic or inorganic filler, that is directly in the course of the synthesis of the polymers[5]. The polymerisation processes in this case can be initiated by complex catalysts, organometallic compounds, free radicals, or ions, fixed on the surface. As a result of the polymerisation of the monomer on the surface of the filler, the latter is covered by a layer of polymer, that is a polymeric capsule is in fact formed[4-6].

The method of polymerisation filling opens up extensive possibilities for the synthesis on filler surfaces of various polymers (homo- and copolymers, block copolymers, two different polymers, etc.).

Control of the kinetics of the process makes it possible to obtain polymer coverings of different thickness, that is compositions with practically any degree of filling (up to 95% of filler by volume). Thus control of the nature of the polymer matrix and the polymer-filler ratio makes it possible to create completely new composition materials which cannot be obtained by ordinary mixing methods.

Work on the synthesis and study of new types of polymer compositions, norplasts, is now being actively developed under the direction of N.S.Enikolopov in the Institute of Chemical Physics of the Academy of Sciences of the USSR and other research establishments in the Soviet Union. These studies are combined in a complex directed scientific and technical programme. A review of work on polymerisation filling using radical polymerisation was published recently[7]. The polymerisation of styrene on the surface of various materials has been studied[8-10].

In recent years, work on the development of a method for introducing fillers into polymers at the synthesis stage has also begun in other countries. Thus the firm of Dupont (USA) has published a series of studies on the polymerisation filling of super-high-molecular polyethylene by inorganic fillers[11].

The overall process of the production of a polymerisation-filled composite consists of three main stages: 1) the preparation of the filler, 2) the production of active centres on its surface, and 3) the polymerisation of the monomer on the surface. The present review examines methods for activating the surface of fillers, mainly using metal-complex and organometallic catalysts. The characteristic features of the kinetics of the polymerisation of monomers, mainly alkenes, on activated fillers, the structure of the materials formed, and their physicomechanical properties have been discussed.

II. PRINCIPLES OF THE POLYMERISATION FILLING OF THERMOPLASTICS

1. Methods for Activating the Surface of Fillers

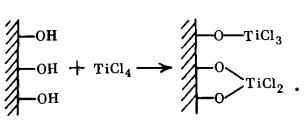
The activation of a filler involves the creation on its surface of active polymerisation centres; this can take place by an ion-coordination, radical, or ionic mechanism.

The preparation of a filler for polymerisation filling by ion-coordination polymerisation involves the removal, from its surface or from the bulk of the filler, of compounds which inhibit the polymerisation process. These compounds include H_2O, O_2, CO_2, CO, SO_2, NH_3, etc. A large number of hydroxide groups or a high acidity of the surface may also lead to retardation of the polymerisation process. In chemical technology, various methods have been developed for the thermal treatment and for the removal of oxygen from dispersed materials. For example, it is possible to use vacuum treatment, azeotropic drying, and sweeping with inert gases under different temperature conditions. From the viewpoint of the technology of removing inhibiting impurities, it is appropriate to use dispersed materials such as perlite, porous glass, Keramzit (light-weight aggregate), cement dust, etc., whose production involves high-temperature treatment. These fillers contain a minimum amount of moisture and hydroxide groups. Their subsequent treatment involves chiefly the removal of oxygen.

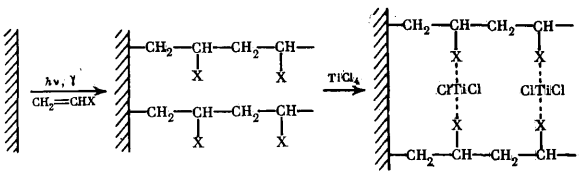
To carry out polymerisation filling by ion-coordination polymerisation, it is necessary to fix metal-complexes or organometallic catalysts on the surface of the filler. Methods have been developed[12,13] for fixing these catalysts, and the methods can be divided into two groups: physical and chemical. In the first case, precipitation (by different methods) of transition metal compounds leads to the formation of a solid phase of transition metal derivatives on the surface or in the pores of the filler. These processes may be accompanied by reduction or oxidation of the transition metal, and they do not require the presence of functional groups on the filler surface. A strong bond is formed between the solid phase of the transition metal compound ($TiCl_3$, VCl_3) and the filler, and this bond is not broken during polymerisation filling. The presence of the solid phase is particularly important for the production of stereoregular polymers such as polypropylene.

The physicomechanical properties of compositions based on polypropylene are determined to a large extent by the ratio of the isotactic and atactic fractions in the polymer. It is therefore necessary to obtain catalysts, fixed on the surface of the filler, which have not only a sufficiently high activity but also a high stereospecificity in the polymerisation of propylene. Of various methods for fixing titanium chlorides on the surface of fillers to act as highly stereospecific catalysts in the polymerisation of propylene, the most promising was found to be the reduction of $TiCl_4$ by organoaluminium compounds on the filler surface[14]. When this method is used, the $TiCl_3$ phase is formed on the surface of the fillers, including those which do not contain functional groups. It is possible to vary both the quantity of titanium fixed and the type of crystallographic modification[14]

Chemical methods of fixing are based on the reaction of transition metal compounds or organometallic compounds with reactive groups on the surface. The surface of an inorganic filler may carry hydroxide groups, whose surface density is easily controlled by thermal and chemical treatment[15-17]. The magnitude of the surface concentration of OH groups is reflected in the nature of the fixing of the catalytic systems. By appropriate reactions, OH groups can be converted into active polymerisation centres, for example:



Analogous processes take place in the case of compounds of other transition metals. If the surface has no reactive groups, it can be made functional by seeding the surface with small quanities (0.1–2%) of monomers with functional groups, using the published method[18]. These methods are convenient in the production of polymer–polymer compositions by the synthesis of one polymer on the surface of another.



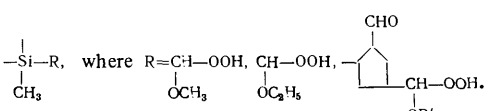
The use of mineral fillers containing catalytically active impurities is of interest. For example, heated kaolin is catalytically active in the polymerisation of ethylene, because of the presence of TiO_2.[11]

The subsequent reaction of transition metal compounds, fixed to the surface, with organometallic compounds (AlR_2Cl, LiR, AlR_3) leads to the formation of active centres, which bring about polymerisation on the surface in the gas phase or in liquid media.

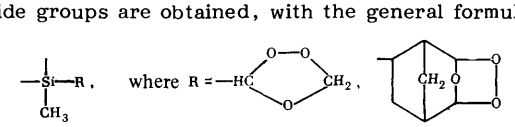
Organometallic compounds of the transition metals can be used for the polymerisation filling of polyethylene[19]. These catalysts have a high activity, and do not require additional activation in the polymerisation medium by an organoaluminium cocatalyst. The formation of the active component in these catalysts takes place by the reaction of the organometallic compound with the surface hydroxide groups of the filler. Compounds of the type $(E{-}O{-})_x{-}MR_y$, where E = Si or Al, M is a transition metal, and R = C_3H_5, $CH_2C_6H_5$, BH_4, etc., are formed on the surface. Filled polyethylene can be obtained using one-component catalysts (for example $TiBz_4$) deposited on natural oxide fillers: asbestos, perlite, alumina, belite sludge, etc.[19]. A high catalytic activity is observed when organic and hydride compounds of zirconium are used.

The dependence of the quantity of catalyst fixed on the conditions under which the process is carried out has been studied[19,20,22]. In the chemical fixing of transition metal derivatives, the limiting quantity of fixed metal is restricted by the number of reactive functional groups on the surface, and for swollen perlite, for example, it amounts to 0.04–0.05% of the mass of perlite. With physical methods for the deposition and formation of the transition metal compound phase on the surface, the quantity of catalyst may be appreciably higher[20,21].

In polymerisation filling processes taking place by a radical mechanism, use is made of fillers which are peroxide group carriers (dialkyl, hydroperoxide) or fillers with groups on their surface capable of polymerisation[23-26]. Comparatively simple methods have been proposed for obtaining peroxide-containing mineral fillers with the general formula:



A mineral filler containing vinylmethylsilyl or norbornenylsilyl groups has been ozonised in alcohol or an organic acid. When the ozonisation is carried out in a hydrocarbon or a halogen derivative, peroxidised fillers with grafted ozonide peroxide groups are obtained, with the general formula



At increased temperatures, these mineral carriers initiate the process of heterogeneous radical polymerisation.

Active polymerisation centres can also be produced on the surface of inorganic fillers by various mechanical and physical treatments of the fillers. Thus the activating effect of thermal treatment and thermal vacuum treatment, and also mechanical grinding[27,28], are familiar in heterogeneous catalysis. The appearance of active centres when various oxides are heated may also be related, for example, to the formation of compounds of the Lewis acid type on the surface, and also to the production of coordinatively unsaturated metal atoms.

Irradiation using different forms of radiation can also be employed to initiate on a surface centres for the polymerisation of such monomers as vinyl chloride, vinyl acetate, acrylonitrile[29], and others, polymerising by a radical mechanism. In addition, these centres can react with organometallic compounds or metal-containing monomers, leading to the formation of ion-coordination centres[30].

2. Regular Kinetic Features of the Polymerisation Filling Process

The regular kinetic features of the polymerisation filling of polyalkenes are determined by the characteristic features of the polymerisation processes on the solid surfaces. Organometallic catalysts, particularly catalysts based on compounds of transition metals in a higher oxidation state, are unstable, and this is revealed in the appreciably non-stationary kinetics of the polymerisation of alkenes in their presence. The fixing of organometallic catalysts on a filler surface usually leads to appreciable stabilisation of their activity with time, and this makes it possible to increase the temperature range in which these catalysts can be used in polymerisation processes[20,21,31] and to increase their efficiency.

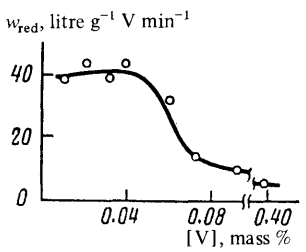


Figure 1. Dependence of the reduced rate of the gas-phase polymerisation of ethylene on the surface of perlite activated by VCl_4 and $Al(i\text{-}C_4H_9)_3$ on the quantity of vanadium fixed on the perlite surface; polymerisation temperature 87 °C, ethylene pressure 2.1 atm.[20]

Increase in the quantity of a transition metal (vanadium or titanium) fixed on a filler surface within the limits of the maximum possible number of reactive functional groups of the same type (for example up to ~6×10^{-6} mole M m^{-2} in the case of swollen perlite) is accompanied by a proportionate increase in the rate of polymerisation of ethylene; the specific activity of the catalyst remains constant (Fig.1). The similarity in the nature of the active centres produced with increase in the surface concentration of the catalyst to the limit given is also indicated by the fact that the observed rate constants of the deactivation of the active centres practically coincide (Table 1).[20,21]

With increase in the surface concentration of the fixed transition metal compound above the limit indicated, the formation of the solid catalyst phase begins, leading to a decrease in the specific catalytic activity of the system in the polymerisation of ethylene (see Fig.1). This is due on the one hand to a change in the nature of the active centres and on the other hand to a simultaneous decrease in the degree of utilisation of the transition metal in the polymerisation process.

Table 1. Kinetic characteristics of the gas-phase polymerisation of ethylene on the surface of inorganic fillers activated by VCl_4; cocatalyst $Al(i\text{-}C_4H_9)_3$.[21]

Catalytic system	[V], mass %	T, °C	w_{red}, litre min^{-1}g^{-1} V	E_{eff}, kcal mole^{-1}	k_d, min^{-1}
VCl_4/perlite	$7.1 \cdot 10^{-3}$	87	38	11.0	$1.8 \cdot 10^{-1}$
VCl_4/perlite	$3.6 \cdot 10^{-2}$	87	43	11.3	$1.5 \cdot 10^{-1}$
VCl_4/aluminosilicate	$8.5 \cdot 10^{-3}$	82	52	11.6	$4.8 \cdot 10^{-2}$
VCl_4/aluminosilicate	10^{-1}	82	16	11.8	$4.5 \cdot 10^{-2}$

Symbols: [V] is the quantity of fixed V, w_{red} the rate of polymerisation, related to the concentration of the monomer and the quantity of catalyst, E_{eff} the effective activation energy of the polymerisation of ethylene, and k_d the rate constant of the deactivation of the active centres in the initial section of the kinetic curve.

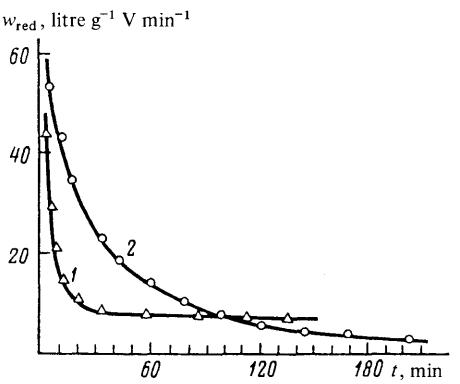


Figure 2. Kinetic curves for the gas-phase polymerisation of ethylene on the system VCl_4/perlite (5.9×10^{-6} g-atom V m^{-2} perlite) (1) and VCl_4/aluminosilicate (8.8×10^{-6} g-atom V m^{-2} aluminosilicate) (2); cocatalyst $Al(i\text{-}C_4H_9)_3$; molar ratio Al/V = 9.2, polymerisation temperature 87 °C, ethylene pressure 2.1 atm.[20]

The mineral materials used as polymer fillers generally have a complex chemical composition. For example, fillers based on SiO_2 or Al_2O_3 contain traces of the oxides of a number of other metals, and this should naturally influence the catalytic properties of the systems formed when catalysts for polymerisation processes are attached to these fillers. As shown in Fig.2, in the gas-phase polymerisation of ethylene

on VCl_4 fixed on perlite and on an aluminosilicate, at similar surface concentrations of vanadium, other conditions of the process being equal, the maximum specific rates of polymerisation have similar values. The stabilities of the catalytic systems formed on perlite and on an aluminosilicate differ considerably, however. For perlite, after an initial non-stationary region, the rate of polymerisation remains constant for a long time, and the kinetics of polymerisation can be described assuming the existence of two types of centre, one of which is deactivated by a first-order reaction, while the second is stable. When an aluminosilicate is used as a filler, the active centres in the initial range are deactivated much more slowly (see also Table 1), the stationary state in general is not reached, and the deactivation law is more complex[20,21].

The increased stability of fixed metal-complex catalysts compared with colloidally dispersed catalysts makes it possible to synthesise polymerisation-filled polyethylene at higher temperatures than usual, up to at least 100 °C.[21] The effective activation energy of the polymerisation of ethylene on the surface of fillers activated by titanium and vanadium compounds is 11.0–11.8 kcal $mole^{-1}$ for both the gaseous and the suspension methods of carrying out the process. As shown by a published analysis[21], the decrease in the rate of polymerisation with time, observed in the processes studied, is not related to diffusion restrictions in the transport of the monomer through the polymer covering to the active surface of the filler, but is due to chemical factors. The transformations leading to the deactivation of the active centres are generally reactions of first order with respect to the active centres. Bimolecular disappearance of the active centres fixed on a surface is seldom observed in the polymerisation of alkenes.

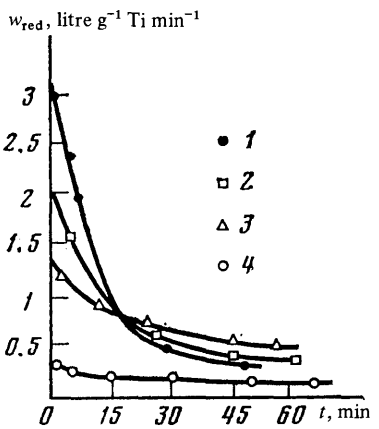


Figure 3. Kinetic curves for the polymerisation of propylene in the liquid monomer for different methods of producing the catalyst on the perlite surface (cocatalyst concentration $[(C_2H_5)_2AlCl] = 4 \times 10^{-3}$ M, polymerisation temperature 70 °C); *1*) β-$TiCl_3$ (reduction of $TiCl_4$ on perlite treated with $(C_2H_5)_2$.AlCl, at 20 °C, 1.5 mass % Ti); *2*) $TiCl_3$ (reduction of $TiCl_4$ on perlite from the complex $TiCl_4$–$(C_2H_5)_2AlCl$, at −45 °C, 2.4 mass % Ti); *3*) $TiCl_3$ (obtained from catalyst 1 by subsequently heating to 180 °C, 1.5 mass % Ti); *4*) $TiCl_3$ (reduction of $TiCl_4(C_2H_5)_2AlCl$ at 180 °C without treatment with $(C_2H_5)_2AlCl$, 1 mass % Ti).[14]

For the polymerisation of propylene on filler surfaces, fixed phase catalysts based on MCl_3 (M = Ti, V) are used[14]. Studies have shown that the level of activity achieved, and the nature of the kinetic curves, depend on the conditions of the formation of the catalyst on the surface of a given filler and on the conditions of the propylene polymerisation process. This is effectively illustrated by the data given in Fig. 3.

The activity of catalysts for the polymerisation filling of polypropylene for a number of fillers studied was found to be higher than that of finely dispersed crystalline titanium trichloride[14].

As in the polymerisation of ethylene, the nature of the filler has a significant influence on the catalytic properties shown by the resulting fixed systems in the propylene polymerisation process[14,32]. The results obtained using graphite as filler are particularly noteworthy[32]. The catalyst $TiCl_3$, deposited on graphite, has a higher activity than $TiCl_3$ deposited on other fillers such as perlite, talc, and chalk (Fig. 4). The polypropylene formed in this case has molecular mass of 1.5×10^6. The introduction of hydrogen into the reaction zone makes it possible to control the molecular mass over a wide range without change in the rate of polymerisation, and this makes it possible to obtain extruded and cast forms of filled polypropylene.

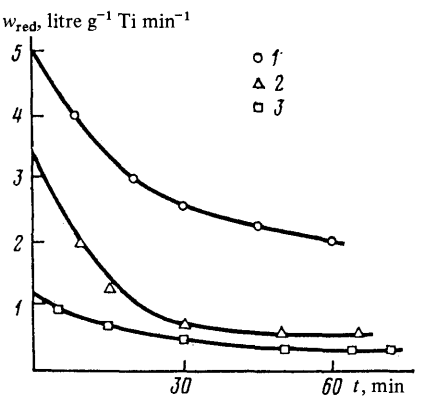


Figure 4. Influence of the nature of the filler on the kinetics of the polymerisation of propylene in the liquid monomer (fixed $TiCl_3$–$Al(C_2H_5)_3$ catalyst, where $[Al(C_2H_5)_3] = 4 \times 10^{-3}$ M, polymerisation temperature 70 °C); *1*) graphite, [Ti] = 0.14 mass %; *2*) perlite, [Ti] = 0.24 mass %; *3*) $TiCl_3.0.33AlCl_3$ (finely dispersed)[32].

The specific activity of a catalyst, based on vanadium and deposited on a filler, in the polymerisation of propylene, as in the case of a catalyst fixed on polymeric catalysts, depends on the surface concentration of the vanadium compound on the filler[33], and this dependence is extreme in character.

Metal-complex catalysts, modified by electron-donating additives and fixed on a surface, can be used to initiate the polymerisation of not only alkenes but also derivatives of vinyl monomers (for example vinyl chloride), whose polymerisation usually takes place by a radical mechanism with the aid of peroxide initiators. This type of polymerisation of vinyl chloride has been carried out[20] using fixed catalysts based on vanadium and titanium chlorides; tri-isobutylaluminium was used as cocatalyst, and diethyl ether was

used as an electron-donating additive. As in the polymerisation of alkenes, the fixing of the catalysts on the surface of the fillers leads to a sharp increase in the efficiency of the polymerisation of vinyl chloride.

The polymerisation of vinyl chloride at first takes place in non-stationary fashion; subsequently, a practically constant rate is established for a long period[20]. The initial non-stationary sections of the kinetic curves, irrespective of the surface concentration of the catalyst, the molar ratio Al/V, and the polymerisation temperature, become complete straight lines on coordinates $1/w-t$. This indicates that the disappearance of the active centres is bimolecular in the polymerisation of vinyl chloride on metal-complex catalysts fixed on a surface, in contrast to the polymerisation of alkenes, where, as shown above, the transformation of the active centres almost always takes place according to the law governing reactions of first order with respect to the active centres. The ratio of the rate constants of the bimolecular disappearance of the active centres and propagation (k_t/k_p) is $(2-3) \times 10^3$, which is characteristic, in principle, of radical polymerisation. The activation energy of polymerisation, determined from the initial reaction rate, is 5.8 kcal mole^{-1}, which is also similar in magnitude to the activation energy of growth in the polymerisation of vinyl chloride by a radical mechanism. On going to the stationary part of the curve, the activation energy of the polymerisation increases considerably (to 11 kcal mole^{-1}), that is to a value characteristic of the ion-coordination polymerisation of vinyl monomers. The polymer formed in the early stages of the polymerisation of vinyl chloride in the production of a polymer covering on the filler particles is characterised by a unimodal molecular-mass distribution (MMD). With further increase in the quantity of polymer in the composite, a second maximum appears on the polydispersion curves in the range of higher molecular masses, and the proportion of the high-molecular-weight polymer increases considerably with time.

The appearance of the bimodal molecular-mass distribution during the process, and the change to stationary polymerisation, might be related in principle to the hetero-phase character of the polymerisation of vinyl chloride in the mass. The second mode, characterising the high-molecular-weight fraction of the polymer, appears, however, even in the initial non-stationary stage of the process, and the ratio of the rate constants k_t and k_p remains constant with time. The observed characteristic features of the kinetics of the polymerisation of vinyl chloride on metal-complex catalysts fixed on filler surfaces can apparently be attributed to the presence of two types of active centre for polymerisation—radical and ion-coordination.

Thus the kinetic studies carried out have established that the catalytic and initiating power of transition metal complexes or organometallic compounds, fixed on a filler surface, is greater than that of the analogous non-fixed systems. This makes it possible to decrease the consumption of catalysts or to obtain a given degree of filling in a short time. Naturally, in the synthesis of highly filled and superhighly filled compositions, the consumption of catalyst per unit weight of the polymer increases. The general regular kinetic features of polymerisation filling are similar to those of the polymerisation of the analogous monomers. The specific features of reactions on a surface, however, raise the question of the reactivity of the associates of the active centres and the transition metal clusters in these systems.

3. Technological Aspects of Polymerisation Filling

Technological studies of the production of polymerisation-filled polyethylene have now been carried out[6,34-36]. Various general questions can be considered. The composition of the material (the degree of filling ϕ) formed in the polymerisation is given by the simple expression[12]

$$\varphi = \frac{P \cdot 100}{\int_0^t w_t dt + P}$$

where P is the quantity of filler introduced into the reaction vessel, and

$$\int_0^t w_t dt —$$

the quantity of polymer formed in the reactor in time t. Thus the degree of filling is determined by the quantity of added filler and the rate and time of polymerisation. The productivity of a continuous reaction vessel g with respect to the overall product will be given by

$$g = \frac{\alpha(P')\bar{y} + P'}{V}$$

where V is the volume of the reactor, P' the quantity of filler added to the reactor in unit time, $\alpha(P')$ the quantity of catalyst on the filler surface, and $\bar{y}$ the specific yield of polymer per unit of catalyst in unit time.

The addition of the filler to the reaction vessel increases the yield of the overall product, and a given concentration of the suspension (Π_p) is reached for a shorter average residence time τ_{av} of the particles in the reaction vessel.

$$\tau_{av} = \frac{\Pi_p}{g} = \frac{\Pi_p \cdot V}{\alpha(P')\bar{y} + P'} .$$

A significant feature is that the productivity of the reactor with respect to the overall product can increase in polymerisation filling without an increase in the heat liberated in the system. If the productivity of the reactor is limited by the limiting concentration of the suspension, it can be seen from the given relationships that this limit is reached in a shorter time when the filler is added to the reactor.

The technological process of polymerisation filling can be carried out under conditions of both gas-phase and suspension polymerisation, and also by polymerisation in the mass of the monomer. The stage of activation of the filler—the fixing of the catalyst or the polymerisation initiator on the filler particles—can also be carried out from the vapour phase of the catalyst in a vacuum or in a stream of an inert gas carrier, or from solution in an organic solvent. Thus the addition of the filler to the polymer at the stage of its synthesis can be organised technologically in such a way that it is entirely gas-phase, entirely suspension, or a mixed version. Necessary requirements for obtaining a product of good quality in all conditions are uniform deposition of the catalyst on all the particles of the filler, and the suppression of the processes of agglomeration of the filler at the stage of catalyst fixing and polymerisation. The latter is important not only from the viewpoint of obtaining the necessary physicomechanical properties of the final material but also to ensure stability of operation of the polymerisation reactor under continuous conditions. The apparatus design for the processes of polymerisation filling is practically the same for the polymer synthesis process. Thus the synthesis of pilot-plant batches of polyethylene–kaolin compositions has been carried out using a technological line for the preparation of high-density polyethylene in the Gur'ev chemical plant[34,36]. A basic diagram of the technological line is shown in Fig. 5. The polymerisation was carried out at 70–80 °C to give 80–70 mass % of polyethylene relative to the added kaolin. The principal parameters of the technological process are given in Table 2.

Analysis of the results of the industrial synthesis of filled polymers has shown that the use of continuous mixing flow reactors has a number of important technological and economic advantages (easy transportation of the suspension, effective removal of the heat of the reaction, the possibility of using existing technological units, etc.). In this case, however, at the outlet from the reaction vessel there will be a certain proportion of particles on which a polymer covering has not been able to form, because of the short residence time in the reactor. The experimental data indicate that the presence of particles not covered by polymer has a significant influence on the quality of the composition, leading to a deterioration in its properties and making processing difficult. This unsatisfactory feature can be eliminated by introducing a grader into the technological line[37]. A mathematical analysis of the possibility of using continuous mixing reactors with pulse introduction of the original reagents and removal of the polymerisation product has been carried out[38]. The analysis showed that this reactor makes it possible to guarantee a given value of the minimum covering of the filler particles by the polymer.

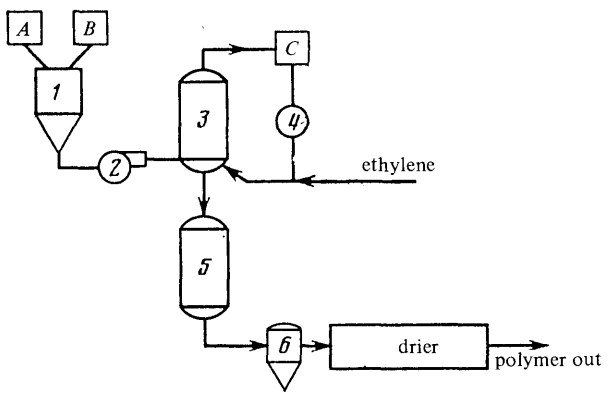


Figure 5. Basic technological scheme for producing a polyethylene–kaolin composition: *1*) vessel for depositing the catalyst on the kaolin surface; *2*) centrifugal pump; *3*) reactor; *4*) gas blower; *5*) product collector; *6*) centrifuge; *A,B*) equipment for metering the components of the catalyst; *C*) cooler[34].

Table 2. Parameters of the technological process[34].

T, °C	τ, h	$P_{C_2H_4}$, kg cm^{-2}	$Q_{C_2H_4}$, kg	c_{H_2}, vol.%
72—80	4.0	2.4—3.2	900	—
70—82	2.0	3.0	550	—
76—78	3.5	2.1—4.0	900	1.2—1.7
73—79	3.0	2.2—3.2	750	6.8

Symbols: τ is the average polymerisation time, $P_{C_2H_4}$ the ethylene pressure in the reactor, $Q_{C_2H_4}$ the quantity of ethylene absorbed, and c_{H_2} the hydrogen concentration in the gas mixture.

The principles of the technological process for the synthesis of porous plastics in the gas phase have been examined[39]. Studies of the kinetic parameters of the process and the removal of heat showed that the gas-phase synthesis of a polyethylene–perlite composition can be carried out under stable conditions.

III. THE STRUCTURE AND PROPERTIES OF POLYMERISATION-FILLED THERMOPLASTICS

1. Some Characteristic Features of the Structure of Polymerisation-Filled Polyalkenes

One of the principal factors determining the properties of filled polymer systems is the nature of the adhesion interaction between the surface of the filler and the polymer. Thus in the production of composite materials the problem is to achieve a strong bond between the polymer matrix and the filler. It is for this purpose, that is to improve the adhesion of the polymer to the filler, that modifying treatment of the fillers and matrix polymers is carried out. There is an extensive literature on the study of the structure and properties of the boundary layers at the surface of separation between the polymer and filler phases, since in the final analysis these determine the principal properties of composite materials[40]. An important contribution to the development of ideas in this field has been made by the work of Lipatov and co-workers[41].

As noted above, in the polymerisation introduction of a filler into a polymer, the centres initiating polymerisation are situated on the surface of the filler particles, and the polymer crystallises directly on the surface or in the pores of the carrier. In a composite material, a chemical bond may be formed between the macromolecules and the surface of the filler[42], or an effective adsorption interaction may be established between them, and this determines the nature of the packing of the macromolecules in the surface layer and the characteristic features of the structure of the boundary layer, and has a significant influence on the physicomechanical properties of the final material.

As a result of polymerisation on the surface, the particles of the filler are covered by a layer of polymer of controlled thickness. Studies carried out by scanning electron microscopy and X-ray spectroscopy[43,44] have shown that the polymer coverings formed under the optimum technological conditions for carrying out the process are uniformly distributed over the surface of the particles, and are compact and continuous. This makes it possible to obtain a fairly homogeneous distribution of the particles of the filler in the polymer matrix in the final composite material.

To increase the area of contact between the filler and the polymer matrix, attempts are usually made to decrease the size of the filler particles, down to fractions of a micron. The processes of agglomeration of the finely dispersed particles of the filler, which always take place, are different for the polymerisation method of introducing the filler and for the mechanical mixing of the prepared components. Thus the optimum dimensions of the particles of the original filler for achieving the required properties of a composite material are determined by the conditions of the process and the nature of the catalytic systems or their components. Thus organometallic compounds and transition metal derivatives may bring about agglomeration or deagglomeration of the particles of the filler during the synthesis of the composite[11].

In polymerisation on the surface of filler particles, the polymer is also formed within the pores, micro-cracks, and defects, so that there is a considerable increase in the area of contact between the filler and the polymer matrix and an increase in the strength of their mechanical interaction.

This is confirmed by scanning electron microscopy, which has been used to study the surface produced by the breakdown of composite specimens[45]. According to the data obtained[45-48], the polymer layer produced during polymerisation on the surface of a filler has an increased density.

It has been shown[45,46] that for identical degrees of filling, composites based on polymerisation-filled polyethylene have a lower coefficient of linear expansion than composites based on mechanical mixtures. This is apparently due to the more compact packing of the macromolecules in the intermediate layer at the polymer–filler boundary in the polymerisation-filled materials. The existence of a compact layer of polyethylene round the particles of filler in norplastics has been demonstrated by other workers[47,48].

X-Ray structural analysis[49] has shown that as a result of the cooperative growth of macromolecules on the surface of fillers, in a number of cases, orientation phenomena are observed in the resulting polymer layer, and the direction of orientation of the molecules corresponds to the normal to the filler surface. These orientation phenomena may be fairly clearly defined. Thus for polypropylene obtained on the surface of organic and inorganic fillers, the extent of the orientation corresponds to that of a polypropylene fibre elongated by a factor of 4–5. The observed orientation phenomena influence the density of packing of the macromolecules in the surface layer and the properties of the boundary layer as a whole.

Calorimetry and X-ray structural analysis indicate that materials based on polyethylene filled during synthesis have a degree of crystallinity which is on the average 10% greater than that of mechanical mixtures with similar compositions and identical characteristics of the polymer matrix[45,46].

These characteristic features of the structure of composite materials based on norplastics are apparently helping to ensure the improvement of the properties of composites relative to mechanical mixtures.

2. Compositions Based on Polyethylene

The use of catalytic systems based on the surface of fillers leads to the formation of high- or superhigh-molecular-weight polymers in the polymerisation process. Polymerisation filling is therefore used to synthesise composites based on a high-molecular-weight polyethylene matrix. Methods have been developed for synthesising polyethylene–kaolin compositions[34,36]. The kaolin was activated using catalysts based on titanium or vanadium in the presence of organoaluminium compounds. Polyethylene–kaolin compositions with a polymer molecular mass of $(1.3-5) \times 10^6$ and containing 30–50 mass % kaolin have good physicomechanical properties. These compositions have no fluidity, and articles are produced by sintering, hot pressing, or extrusion. Superhigh-molecular-weight polyethylene has recently been attracting increasing interest as a material with unique properties, and also as a substitute for Fluoroplast. Polymerisation-filled superhigh-molecular-weight polyethylene has a higher wear-resistance and a higher modulus of elasticity than these polymers. Since it is unlikely that alternative methods for obtaining filled compositions based on superhigh-molecular-weight polyethylene by methods involving mixing will be found, the development of the technology for the synthesis of these compositions by polymerisation filling is an important direction of development in this field.

The molecular mass of the polymer matrix in compositions based on polyethylene (PE) is controlled by the usual methods, by adding hydrogen or other chain transfer agents to the system. Thus in the polymerisation filling of polyethylene by kaolin activated by complex vanadium catalysts, the introduction of 15 vol.% hydrogen leads to a decrease in the molecular mass (MM) of the polyethylene matrix from $(2-3) \times 10^6$ to $(1.2-1.6) \times 10^4$.[50] The fluidity index of a molten polyethylene–kaolin composition with a degree of filling of 30 mass % increases from zero (in the absence of H_2) to 10 when $Al(i\text{-}C_4H_9)_3$ is used as cocatalyst. Thus polymerisation filling using an additive which controls the MM of polyethylene gives composites which can be worked by extrusion.

With decrease in the molecular mass of PE, its degree of crystallinity increases, leading to an increase in the rigidity of the polymer and the composition as a whole, to an increase in the modulus of elasticity and the yield point on elongation, and to a decrease in the relative elongation at the yield point[51].

The extent of the decrease in various physicomechanical characteristics with decrease in the molecular mass of the polymer matrix of a composition depends on the nature of the surface of the filler and on its dispersion composition. For various fillers, compositions have been developed which can be worked by casting and extrusion, and articles with good physicomechanical properties have been obtained ($\sigma_t = 25$ MPa), $\varepsilon = 50-400\%$).

Polymerisation has been used[50] to obtain composites with different concentrations of kaolin over a wide range of MM of the polymer matrix (from 3000000 to 125000). When superhigh-molecular-weight polyethylene with MM $> 10^6$ was used as the matrix, the introduction of a filler into the composition in concentrations up to 50 mass % did not lead to any loss of plasticity by the material. The composite deformation curves show high values of the deformational-strength characteristics. For polyethylene–kaolin compositions containing 0, 30, and 50 mass % filler, the limiting tensile strength (σ_t) is 46, 44, and 23 MPa, ε_t decreases from 260 to 240 and 150%, and the modulus E_t increases from 900 to 1900 and 1900 and 2900 MPa respectively. The filling of low-molecular-weight PE leads to the loss of plasticity by the composite at degrees of filling lower than those for superhigh-molecular-weight PE.

Table 3. Properties of heat-insulating materials obtained from norplastics containing swollen perlite and polyethylene[12].

Material	c_p, mass %	σ_c, MPa	σ_b, MPa	m, kg m^{-3}	λ, kcal m^{-1}s^{-1}K^{-1}
Norplastic perlite–PE	10—12	5—9	3	120—150	0.03—0.04
Perlite–phenol-formaldehyde resin*	70	3—5	3	120—150	0.03—0.05

Symbols: c_p is the polymer concentration, σ_c the compressive strength, σ_b the bending strength, m the volume mass, and λ the thermal conductivity coefficient.

*The properties of a heat-insulating material based on perlite and produced in industry at present are given for comparison.

Polymerisation filling can be used not only to obtain finished composites with a given concentration of filler but also to modify the surface of a filler. This is achieved by producing thin polymer coverings during polymerisation on the particles of the filler, and the process can be regarded as a form of finishing of the surface, using macromolecular chains.

These polymerisation-modified fillers or norplastic "concentrates" can be used as independent superhigh-filled composition materials containing up to 80–95 mass % of a mineral component, for example for the production of heat-insulating materials (Table 3).[12]

In addition, norplastic "concentrates" can be introduced as modified fillers by mixing with a prepared industrial polymer of similar character; in particular, this represents one possible way of obtaining cast and extruded composite products[43,45,52–56]. The use of norplastic "concentrates" is promising, since it makes it possible to obtain materials having better physicomechanical properties than mechanical mixtures with analogous composition. For polyethylene composites, these differences are revealed particularly clearly in the values of the specific impact ductility: this property is 1.5–2 times greater for composites based on polymerisation-modified fillers than for mechanical mixtures[43,56].

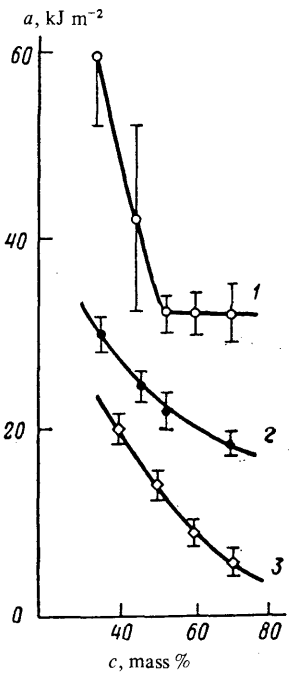


Figure 6. Dependence of the specific impact ductility (a) on the tuff concentration (c) for compositions based on HDPE and tuff (average particle size of the tuff 8.6 μm): *1*) HDPE–norplastic concentrate; *2*) HDPE–tuff–SHMPE mechanical mixture; *3*) HDPE–tuff mechanical mixture[56].

Fig.6 gives the dependence of the specific impact ductility for composites based on high-density polyethylene (HDPE) and a norplastic concentrate containing 87.5 mass % tuff and 12.5 mass % superhigh-molecular-weight polyethylene (SHMPE) on the concentration of tuff in the composite[56]. For comparison, data are given for mechanical mixtures of the matrix polymer and tuff and for mechanical mixtures with the addition of SHMPE in the same quantities as were added in the form of the norplastic "concentrate" to the composites based on norplastics. Results showing differences of a similar scale have also been obtained for composites based on other fillers[43].

The dependence of the tensile strength and the static bending strength on the degree of filling in the composites studied is extremal in character[45,56], and the optimum value lies in the range corresponding to 30–50 mass % filler, depending on the nature of the filler. Fig.7 gives comparative data on the dependence of the maximum tensile strength on the degree of filling for composites with the same composition as in Fig.6. Fig.7 shows that the strength of the composites based on norplastics is much greater than that of the materials obtained by mixing. The use of polymerisation filling also leads to an increase in the rigidity of the resulting material, compared with mechanical mixtures[43].

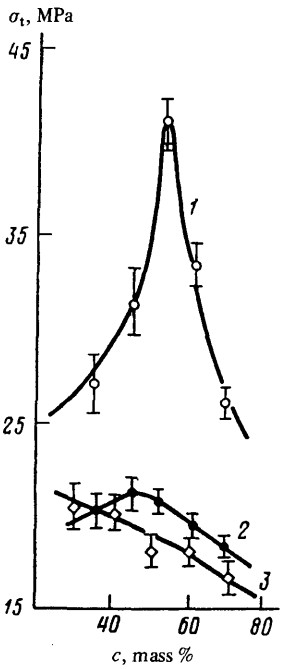


Figure 7. Dependence of the maximum tensile strength (σ_t) on the concentration of filler for compositions based on HDPE and tuff: *1,2,3*) see caption to Fig.6; rate of deformation $\bar{\nu}_\varepsilon = 1.04 \times 10^{-1}$ min^{-1}, σ_t for HDPE = 21.3 ± 1.4 MPa.[56]

Increase to a definite limit in the thickness of the polymer covering which is formed on the particles of the filler and which consists of superhigh-molecular-weight PE leads to an improvement in the strength properties and rigidity of materials based on norplastic "concentrates" for a given concentration of the mineral filler (Fig.8). Fig.8 shows that for the compositions studied, this limit corresponds to ~30 mass % PE in the "concentrate" or ~9 mass % in the composite, for a perlite concentration of 30%. The addition of SHMPE in the same quantities to mechanical mixtures of the matrix polymer and the filler also leads to an increase in the strength of the material, but the properties of the composites obtained in this way are considerably inferior to those of the composites based on norplastics.

3. Compositions Based on Polypropylene

The use of polymerisation filling to introduce fillers into polypropylene (PP) has given new materials with an unusual set of physical and mechanical properties. The structure of polypropylene formed on the surface of a filler is determined to a large extent by the nature of the filler and by the conditions under which the catalyst is prepared and the process is carried out[14,32]. An interesting feature is that the use of graphite as a filler gives the highest degree of isotactic character in PP (up to 94–96%).

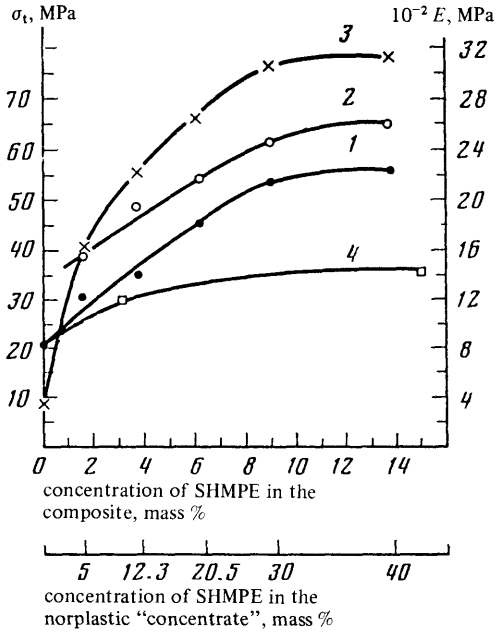


Figure 8. Influence of the concentration of SHMPE in a norplastic concentrate based on SHMPE and swollen perlite on the tensile strength (*1*), the static bending strength (*2*), and the tensile modulus of elasticity (*3*) for compositions based on HDPE and a norplastic "concentrate"; concentration of swollen perlite in all compositions 30 mass %; $\bar{v}_\varepsilon$ = 0.87 min^{-1}; *4*) change in tensile strength for HDPE–perlite–SHMPE mechnical mixtures[43].

The study of the electrical conductivity of polypropylene–graphite compositions has shown that polymerisation filling provides a new and promising method for obtaining heat-conducting and electrically conducting compositions[57–59]. Comparison of the specific resistance of composites obtained by polymerisation filled and mechanical mixtures of polypropylene and graphite shows that for the same degrees of filling, the mechanical mixture has a much lower conductivity (Fig. 9). The conductivity differences are particularly marked (by a factor of 10^7) at low concentrations of the filler $c \leq 8$ vol.%. To obtain by mechanical mixing a composition with the same conductivity, it is necessary to add 30 vol.% graphite, and this leads to a decrease in the tensile strength and compressive strength by factors of 1.5. Composites based on PP and graphite have a high uniformity, as indicated by the linear dependence of σ on the length and thickness of the specimen. In the temperature range 4.2–300 K, the values of σ for polymerisation-filled compositions are independent of temperature (for composites containing 8–61 vol.% graphite)[57] (Fig. 10). For these compositions, a conductivity constant with time was observed for graphite concentrations $c \geq 8$ vol.%, whereas for the compositions obtained by mixing this was observed only at $c \geq 20$ vol.%.

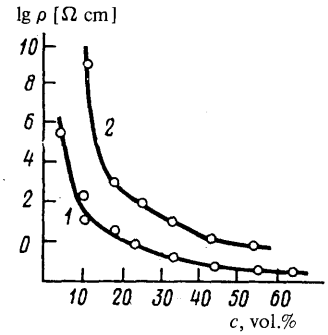


Figure 9. Dependence of the bulk specific electrical resistance (ρ) of compositions based on polypropylene and graphite on the graphite concentration: *1*) polymerisation filling, *2*) mechanical mixture of polypropylene and graphite[57].

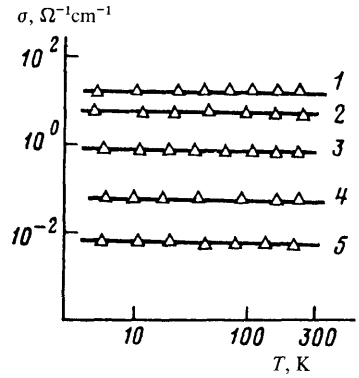


Figure 10. Temperature dependence of the conductivity of polymerisation-filled composites based on polypropylene and graphite for different volume concentrations of graphite: *1*) 0.61, *2*) 0.4, *3*) 0.35, *4*) 0.1, *5*) 0.08.[57]

The materials obtained show another remarkable property, namely their retention of plasticity and mechanical strength after repeated cooling and heating cycles from 300 K to 4.2 K. A scanning electron microscope study of the surface of pressed specimens of norplastics based on polypropylene and graphite showed that the norplastic (for identical original graphite particle sizes) contains graphite particles of smaller dimensions, uniformly distributed in the polymer matrix, compared with the mechanical mixtures, and the distance between the particles of the filler is much smaller in the norplastic.

These composites based on polypropylene and graphite are promising for applications in many branches of technology, as elements in electric-heating assemblies, coverings for screens in radio-electronic apparatus, strain gauges at low temperatures, highly stable resistors, antistatic coverings, and electric filters[60].

The strength properties of norplastics based on PP with a degree of filling of 30–40% are similar to those of non-filled isotactic polypropylene[32]. The presence of an atactic polypropylene fraction in the composite (up to 10–15%) has a plasticising influence and improves the deformational properties of the compositions.

Isotactic polypropylene has a low resistance to cold. To improve this property, rubber is added to polypropylene, or copolymerisation with ethylene is carried out. The use of polymerisation to introduce fillers into PP has made it possible to produce, on the basis of filled polypropylene, materials having a high resistance to cold (brittleness temperature between −35 °C and −45 °C) and a high impact strength (up to 18 kJ m^{-2}) at a concentration of filler (tuff, kaolin) of 40–50 mass %.[5]

4. The Thermo-Oxidative Degradation and Stabilisation of Norplastics

The kinetics of the thermo-oxidative degradation of polymerisation-filled polyethylene and mixed compositions at temperatures of 160–200 °C and oxygen pressures of 24×10^3–27×10^3 Pa have been studied[61]. Inhibitors were introduced into the powdered composite from a solution in ethanol or toluene, after which the powder was dried in a vacuum. The principal rapid method used to estimate the effect of the inhibitors was a volumetric method involving the measurement of the absorption of oxygen by the specimen on heating under static conditions. As with polyethylene, irrespective of the nature of the filler, the introduction of the inhibitor leads to a significant increase (by a factor of 3–7) in the induction period, and a decrease (by a factor of 1.5–3) in the rate of oxidation of the composite. The greatest increase in the induction period and decrease in the rate of oxidation were observed at concentrations of Irganox 1010 corresponding to 0.1–0.15% of the total mass of PE in the composite. The best results for composites containing any filler, however, were obtained using a synergic mixture of Irganox 1010 and Irganox PS 802. When fillers containing metallic components are used, and with specimens used at high temperatures in contact with a metal surface, it is necessary to add metal deactivators to the inhibitor mixture.

5. Compositions Based on Other Polymers

Among other thermoplastics, the polymerisation filling of polyvinyl chloride (PVC) is of greatest interest. The grafting of PVC macromolecules to the surface of fillers during radical polymerisation makes it possible to obtain "concentrates" which when mixed with PVC give a composite with much better properties than compositions based on non-modified fillers[42]. Both the technological properties and the strength characteristics are improved. In addition, the chemical grafting of PVC to the surface of fillers may be an important factor in obtaining composites with long-term strength.

Problems related to the radical mechanism of polymerisation initiated on the surface of a solid phase and to the characteristic features of radical copolymerisation taking place on the surface of solid particles have been examined[25,26]. The studies established that it is possible to vary widely the characteristics of the graft polymers: the molecular mass, the density of grafting, and the ratio of the grafted and non-grafted polymers in relation to the parameters and methods of polymerisation. When there are no reactions of chain transfer, it is possible to obtain polymerisation-filled compositions in which practically all the macromolecules are grafted to the surface of the dispersed filler. As a consequence of the formation of the chemical bond between the polymer and the filler, these polymerisation-filled polymers have higher wear-resistance, creep-resistance, and strength properties, compared with polymers filled by traditional methods. The industrial production of polymers filled by polymerisation under radical-polymerisation conditions can be carried out in existing equipment used for polymer synthesis[7].

The development of methods for the polymerisation filling of reactive carbo-chain polymers is also important. These include polymers obtained by the homo-polymerisation of propadiene and acetylene derivatives, and their copolymerisation with alkenes. Propadiene polymerises in the presence of metal-complex catalysts[62] based on vanadium, titanium, nickel, and rhodium. The use of transition metal salts as catalysts makes it possible to use polar solvents such as water and alcohol for the polymerisation of propadiene. In the presence of a catalyst based on rhodium acetylacetonate carbonyl in a medium of ethanol, the polymerisation is non-stationary (Fig. 11). After an induction period, the reaction rate increases and reaches a maximum value, after which almost complete deactivation of the catalyst takes place. The deposition of this catalyst on the surface of swollen perlite leads to an increase in the activity and stability of the catalyst. The rate of the polymerisation of propadiene is higher when the deposited catalyst is used, and remains unchanged for a long time. The increase in the stability of the catalyst deposited on the filler surface is due to a decrease in the rate of the reactions involving the disappearance of the active centres taking place in the solutions.

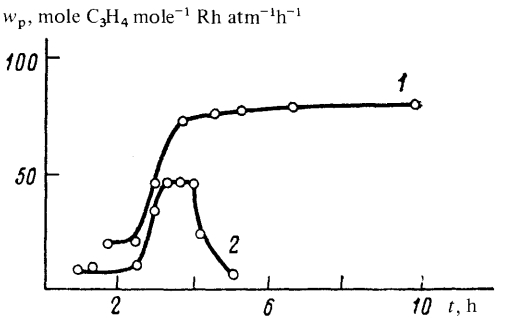


Figure 11. Change with time in the rate of polymerisation of propadiene on $Rh(AcAc)(CO)_2$ fixed on perlite (*1*) and $Rh(acac)(CO)_2$ in C_2H_5OH (*2*).[62]

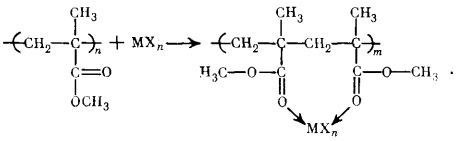
Similar kinetics are observed in the polymerisation of phenylacetylene in the presence of $MoCl_5$ fixed on kaolin, talc, and aluminium and magnesium oxides[63]. The fixing of $MoCl_5$ on mineral carriers leads to an increase in the lifetime of the catalyst and to an increase in the degree of transformation of phenylacetylene. The nature of the mineral carrier influences the stereospecificity of the catalyst and the molecular mass of the polymer.

The products obtained by the polymerisation filling of propadiene and acetylene derivatives can subsequently be cross-linked by various methods.

6. Polymer–Polymer Compositions

The immobilisation of metal-complex catalysts on carbo-chain polymers makes it possible, by using a polymer carrier as filler, to synthesise polymer–polymer compositions (PPC) at the stage of the polymerisation or copolymerisation of alkenes, and this represents a further development of the method of polymerisation filling[64]. The polymeric fillers used include polyvinyl chloride, polyvinyl acetate, polymethyl methacrylate (PMMA), polyformaldehyde, cellulose, and other polymers.

The fixing of MX_n to the surface of such polymers as polymethyl methacrylate or polyvinyl acetate can be represented as follows:



The process is accompanied by a displacement of the carbonyl group stretching frequency from 1740 cm^{-1} to 1650 cm^{-1}.[64] The fixing of MX_n to polyvinyl acetate takes place similarly. The mechanism of the interaction of MX_n with cellulose is more complex, and leads to cross-linking of the cellulose molecules.

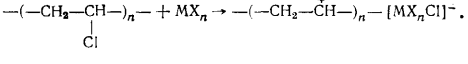
Table 4. Physicomechanical properties of PE–PMMA polymer–polymer compositions and the original components (upper values—data for the synthetic PPC, lower values—data for the mechanical PPC).[64]

Parameter	PMMA*/PE	[PMMA], vol.%			
		4	7	14	29
ρ, kg m^{-3}	1.190 / 0.948	0.959 / 0.962	0.968 / 0.965	0.983 / 0.965	1.019 / 1.017
σ_y, kg mm^{-2}	5.0 / 2.50	3.20 / 2.70	3.15 / 1.20	3.50 / 1.15	—
ε, %	2—3 / 370	250 / 80	210 / 70	180 / 45	—
T_g, K	383 / 203	217 / —	224 / 224	224 / 224	225 / 224

Symbols: ρ is the density, σ_y is the yield point, ε the elongation at rupture, and T_g the temperature of glass formation.

*This column gives the corresponding values of the parameters of the original components of the polymer composition.

Of particular interest is the fixing of MX_n on the surface of polymeric carriers containing a mobile halogen atom: copolymers of PVC, polyvinylidene chloride (PVDC), polytetrafluoroethylene (PTFE), copolymers of styrene with α-bromostyrene, etc. In these cases, the fixing involves the formation of ionic products:



The synthesis of PPC based on polymers activated by these methods is carried out by ordinary polymerisation methods. The physicomechanical properties of synthetic and mechanical PE–PMMA and PE–PVC compositions are compared in Tables 4 and 5. Increase in the volume fraction of PMMA in the composition with PE is accompanied by a decrease in the relative elongation and an increase in the yield point of the compositions. The synthetic PPC have much better physicomechanical properties than the corresponding mechanical compositions. The difference is particularly marked at high values of ϕ.

Table 5. Various properties of PE–PVC polymer–polymer compositions and the original components (upper values—data for the synthetic PPC, lower values—data for the mechanical PPC).[64]

Parameter	PE*/PVC	PE/PVC, mass %				
		83/17	77/23	70/30	56/44	45/55
σ_t, MPa	30.1 / 42.0	22.0 / 24.2	16.2 / 14.4	21.3 / 5.0	20.3 / —**	16.8 / —
ε, %	40.0 / 23.0	80.0 / 8.5	30.0 / 5.0	20.0 / —	62.5 / —	13.0 / —
r, kN m^{-1}	52 / 30	19 / 3.0	30 / 3.5	17 / 3.5	25 / —	31 / —

Symbols: σ_t is the limiting tensile strength, ε the relative elongation, and r the tear-resistance.

*Corresponding values of the parameters of the original components of the composition.
**Brittle specimens; the properties could not be determined.

In PPC obtained by mechanical mixing, the intermediate layer is formed by the mutual diffusion of the polymers. In the synthetic PPC, the production of the intermediate layers involves not only physical but also chemical interactions.

According to a model[64] in which there are no interactions at the boundary of separation between the phases, the following relationship should be observed between the yield point of polyethylene (σ_0), σ_{PPC}, and the volume fraction of polyethylene ϕ:

$$\sigma_{PPC}/\sigma_0 = 1 - \varphi^{2/3}.$$

Fig. 12 shows that in mechanical PPC based on polyvinyl chloride and polyethylene, there is satisfactory agreement between the experimental data and the theoretical relationship. This relationship is not observed for the synthetic compositions, indicating the existence of specific interactions between PE and PVC. One factor responsible for chemical interaction between the two polymers may be the grafting of polymer chains during the synthesis of the PPC. The presence of grafted chains in synthetic PE–PMMA and PE–PVC compositions has been established by physicochemical and extraction methods[64]. Mechanical PPC may undergo complete breakdown into the original components. The concentration of grafted polymer chains in the synthetic PPC depends on the type and volume fraction of the polymers. For example, with increase in the volume fraction of the vinyl polymer, the degree of grafting increases in the PE–PMMA system, and decreases in the PVC–PE system[64]. The mutual grafting of chains during the synthesis of polymer–polymer compositions may take place at the initiation stage, at the growth stage by the copolymerisation of unsaturated units,

and by reactions involving chain transfer at the surface of the basic polymer.

The formation of the intermediate layer may be influenced by the physical interweaving of the linear macromolecules with the open network of the surface. An X-ray diffraction study of synthetic polymer–polymer compositions based on PMMA–PE and PVC–PE has revealed changes in the values of the interplanar distances in the structures of synthetic compositions[65]. This indicates a reaction between the PE and the other polymers in synthetic compositions at the molecular level.

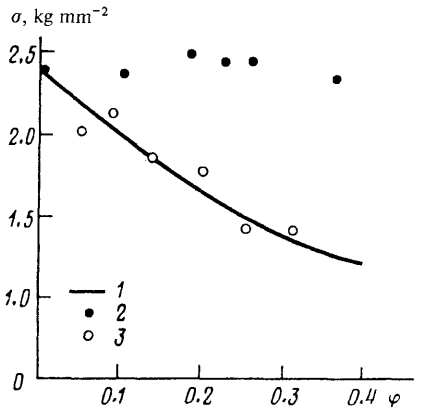


Figure 12. Dependence of the yield point of PPC based on PE and PVC on the volume fraction of the latter: *1*) theoretical curve; *2*) mehcnical PPC; *3*) synthetic PPC.[64]

Thus the synthetic method for preparing PPC makes it possible, at the stage of the synthesis of the polyalkene component, to increase the compatibility of the components as a result of the characteristic treatment of the surface, and to some extent to restrict or suppress the negative effects characteristic of mechanical methods for prepared PPC. This method can be used to obtain composition materials based on polymers which are not readily compatible under ordinary conditions.

IV. CONCLUSION

Examination of studies carried out up to the present, and the results obtained, shows that the method of polymerisation filling extends considerably the possibilities for creating composite materials for different purposes, including constructional purposes, on the basis of the filled polymers.

This is determined by many factors, including the wide synthetic possibilities of the method, the possibility of controlling over a wide range the composition of the products with the achievement of exceptional uniformity of the distribution of the particles of the fillers in the polymer matrix, the possibility of fine control of the structure of the compositions, and the improvement of the adhesion interaction at the surface of separation between the filler and the polymer phases, either as a result of chemical bonding between the macromolecules and the surface of the filler or as a result of the development of an effective adsorption interaction between them. Essentially, Enikolopov and his school have developed a new branch of macromolecular chemistry, involving the study of the specific features of the kinetics of polymerisation on solid surfaces, the characteristic features of the structure of the polymeric layer formed on the surface of fillers during polymerisation, the characteristic features of the physicomechanical properties of composites, and the working of these materials.

A number of promising ways of using the polymerisation filling of thermoplastics have now been established: the synthesis of highly-filled compositions based on superhigh-molecular-weight polyethylene, the synthesis of "concentrates" containing ~10% of the polymer matrix, and the synthesis of highly conducting and cold-resistant compositions based on polypropylene. New phenomena requiring further intensive study have been observed. The production of a composite material with given properties naturally requires the solution of complex problems both in the synthesis of the polymers and in the physics and mechanics of the compositions. Specific fields of application of polymerisation-filled materials and realistic possibilities for the development of industrial processes for their production have already been pointed out, however.

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Institute of Chemical Physics,
Academy of Sciences of the USSR,
Moscow

Translated from *Uspekhi Khimii*, 53, 223-235 (1984) U.D.C. 66.095.264 + 546.73

Metalloporphyrins as Catalysts of Chain Transfer in Radical Polymerisation and Stereoselective Oxidation

L.V.Karmilova, G.V.Ponomarev, B.R.Smirnov, and I.M.Bel'govskii

The results of studies on the catalysis of the chain transfer reactions in radical polymerisation and stereoselective olefin oxidation reactions in the presence of metalloporphyrins are surveyed. The problems of the synthesis of metalloporphyrins for catalytic studies are discussed.
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I. INTRODUCTION

Studies of the catalytic properties of porphyrins and related macrocyclic compounds have developed vigorously in recent years. The interest in these compounds is due primarily to the fact that their metal complexes are involved in the most important processes in living nature—photosynthesis and the transport, fixation, and activation of oxygen.

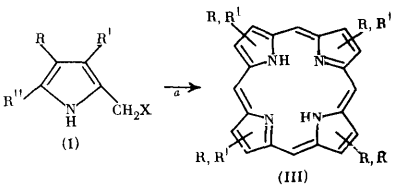
The principal results of studies, carried out under the overall supervision by N.S.Enikolopov, on the synthesis of porphyrins, the catalytic methods for the regulation of radical polymerisation with the aid of metal complexes, the synthesis and properties of immobilised catalysts, and the catalysis of stereoselective oxidation are summarised in this review.

II. THE SYNTHESIS OF PORPHYRINS FOR CATALYTIC STUDIES

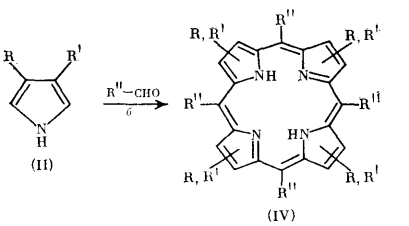
The advances in physicochemical and biological researches into metalloporphyrins as well as the possibility of their practical employment as catalysts of various processes, dyes, medicinal preparations, etc. have been to a large extent determined by the level of synthetic developments in this field. Towards the beginning of the 1980's, extremely advanced methods were developed for the synthesis of asymmetric porphyrins based on the successive addition of pyrrole fragments with subsequent cyclisation, which made it possible to obtain compounds with virtually any specified structure. The achievements in this field of the porphyrin chemistry have been summarised in a review by Evstigneeva[1] and in a fundamental work edited by Dolphin[2]. However, compounds simplified to the maximum extent rather than complex multifunctional compounds are required for the purposes of the photochemistry, electrochemistry, analytical chemistry, kinetics, catalytic action, and the study of the reactivity of tetrapyrrole macrocycles. These compounds must contain a definite set of alkyl or aromatic substituents and must be readily soluble in water or organic solvents. The principal requirements which must be met in the synthesis of compounds to be used for practical purposes is ready availability of the starting materials and the existence of a technological procedure for the synthesis and purification of the required porphyrins.

The development of studies in the field of the synthesis of porphyrins as potential catalysts proceeded via the preparation of derivatives with functional substituents, based on simple and ready available octa-alkylporphyrins and meso-tetra-arylporphyrins, and also via the improvement of technological schemes for the isolation and modification of porphyrins from readily available natural sources—haemin and chlorophyll.

Symmetrically substituted porphyrins are usually synthesised in a single stage via the cyclotetramerisation of 2,5-disubstituted pyrroles (pathway *a*) or via the condensation of 2,5-unsubstituted pyrroles in the presence of aldehydes (pathway *b*)[2]:



R, R' = Alk; R'' = H, COOH; X = OH, NH_2, $N(CH_3)_2$

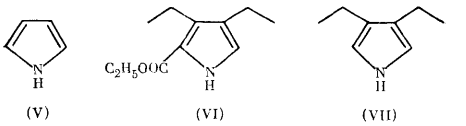


R, R' = H, Alk, R'' = Alk, Ar, 4(3)-pyridyl

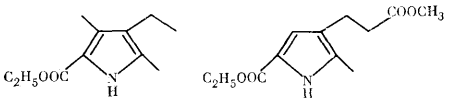
The exact positions of the groups R and R' in the porphyrins are not indicated in view of the formation of a racemic mixture of isomers when $R \neq R'$.

The synthesis of octa-alkylporphyrins (III) from the pyrroles (I, R, R' = Alk, R'' = COOH, X = OCH_3) is possible via pathway *a* with a yield of 70–80%. Pathway *b* leads to porphyrins (IV) in 70–80% yield when R, R' = Alk and R'' = H and 50–60% when R'' = Ar.

For practical requirements, it is possible to confine oneself to an extremely small number of initial pyrroles, whose employment makes it possible to solve the majority of problems in the synthesis of simple porphyrins. One such compound is the pyrrole (V), from which the preparation of *meso*-tetra-aryl(pyridyl, alkyl)porphyrins does not present special difficulties. The pyrroles (VI), (VII), and (VIII) are necessary for the synthesis of octaethylporphyrin and aetioporphyrin isomers—the most convenient models in a wide variety of physicochemical studies, while the pyrrole (IX) is used to model porphyrins with the natural structure.

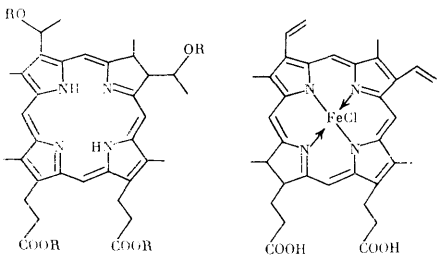


(V) (VI) (VII)

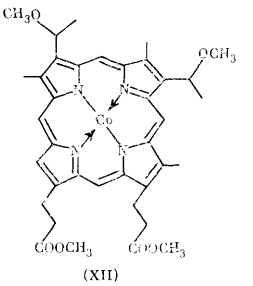


(VIII) (IX)

For an extensive investigation of the catalytic properties of porphyrins and related macrocycles, it was necessary to synthesise porphyrins and metalloporphyrins which would be highly soluble in organic non-polar or weakly polar solvents. For this purpose, an improved method was developed[3] whereby one could readily obtain the "tetra-alkyl ether-esters" (X) of haematoporphyrin, which consists in the successive treatment of the natural haemin (XI) with a solution of HBr in acetic acid accompanied by the addition of the corresponding alcohol to the reaction mixture.



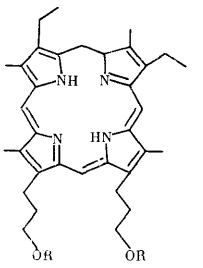
(X) (XI)



(XII)

The metal complexes of the "tetraether-esters", in particular the cobalt complex (XII), are readily soluble in the majority of hydrocarbons and other organic solvents, which made it possible to carry out extensive tests of the catalytic activity and to discover a new phenomenon in the radical polymerisation reactions—the catalytic chain transfer from the radical to the monomer[4].

However, the low stability of the metal complexes of the tetraether–esters significantly hindered their practical employment. A method was therefore developed for the synthesis of the more stable porphyrin (XIII) directly from haemin in yields up to 80%. The interaction of the porphyrin (VIII) with aliphatic acid chlorides, for example, with caprylic acid, makes it possible to obtain the corresponding esters soluble in any non-polar organic solvent and the reaction with acryloyl chloride yields the ester (XIV) which can be used for copolymerisation with methyl methacrylate and other acrylates in order to obtain porphyrin-containing polymers with catalytic activity.

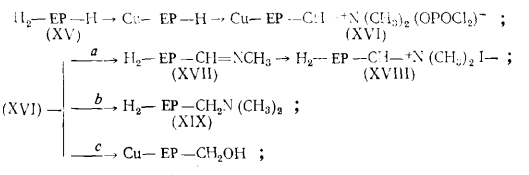


(XIII) R = H
(XIV) R = $COCH{=}CH_2$

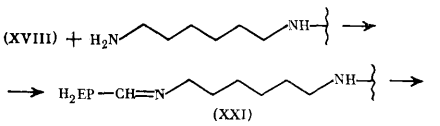
Another branch of studies in the synthesis of porphyrins in order to create catalytic systems involved the preparation of derivatives based on simple and readily available octa-alkylporphyrins and *meso*-tetra-arylporphyrins with functional group substituents.

The presence of a functional group as a substituent makes it possible to vary within wide limits the chemical properties of the porphyrin and also to graft metalloporphyrins to the surface of a solid carrier. Such immobilisation of porphyrin complexes makes it possible not only to create catalysts capable of being used repeatedly but also to increase greatly their concentration, preventing the precipitation from solution of sparingly soluble metal complexes. It has been shown that the use of the Vilsmeier reaction in relation to porphyrins leads to considerable possibilities for the synthesis of a wide variety of compounds containing a functional group substituent in both *meso*- and β-positions in the macroring. The optimum version of the Vilsmeier reaction is not the synthesis of the formylporphyrins themselves but the preliminary preparation of intermediate reactive "phosphate complexes", which are then used to prepare a wide variety of porphyrins with functional group substituents[5–10].

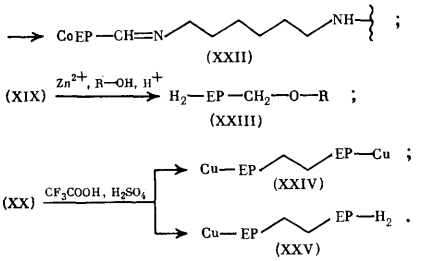
Examples of various reactions of one of the representatives of octa-alkylporphyrins, namely aetioporphyrin-1 (H_2-EP-H) (XV), which are of interest for the synthesis of catalysts, are presented below:



(XX)



(XXI)



Three main versions of the modification of the "phosphate complex" are possible. Pathway *a* permits the synthesis of a wide variety of Schiff bases under mild conditions and with a high yield. For example, the demetallation of compound (XVI) with concentrated H_2SO_4 and subsequent treatment with aqueous methylamine lead to the Schiff base (XVII), whose methiodide (XVIII) readily reacts with aliphatic amines to form Schiff bases in 85–95% yield. The interaction of compound (XVIII) with the "Separon" macroporous gel containing hexamethylenediamine residues leads to the immobilisation of the porphyrin on the surface of the carrier, as in the system (XXI). After the introduction of a cobalt ion into the porphyrin (XXI), a heterogeneous catalyst (XXII) was obtained and its properties were investigated comprehensively[8]. An analogous attachment of a porphyrin was achieved on glass beads and was completed by a finishing treatment with triethoxyaminopropylsilane.

Pathway *b* has not so far been tested in practice, but it is also of interest for the modification and immobilisation of metalloporphyrins. It has been found that the porphyrin (XIX), obtained from the complex (XVI) by reduction with $NaBH_4$ and demetallation in concentrated H_2SO_4, readily reacts with alcohols and CH acids (acetone, acetylacetone, nitromethane, and cyanoacetic or nitroacetic esters) to form the ethers (XXIII) and other compounds.

Finally, pathway *c* makes it possible to obtain the ethane-bisporphyrins (XXIV) and (XXV), containing one or two metal atoms in the molecule, from the complex (XX), formed in quantitative yield after the successive treatment of the complex (XVI) with aqueous alkali and $NaBH_4$. Similar compounds may be of interest in the study of the catalytic activation of simple molecules of the type of O_2, N_2, CO, and CO_2.

Thus, several reliable methods of synthesis of metal complexes of porphyrins, readily soluble in various organic media, are at present available to investigators. This creates extensive possibilities for the comprehensive study of the catalytic properties of such compounds in polymerisation, oxidation, dehydrogenation, and other reactions.

III. CATALYTIC REGULATION OF RADICAL POLYMERISATION

The vast majority of methods for the regulation of radical-chain polymerisation processes are based on the introduction of various inhibitors, moderators, and chain-transfer agents, reacting with the chain carrier radical in stoichiometric proportions close to unity[11]. Thus the regulation of the molecular weight (MW), for example, is achieved as a result of chain transfer reactions via a mechanism involving the abstraction by a macroradical $R_n^{\cdot}$ of individual atoms or fragments from the molecule of the chain transfer agent SX:

$$R_n^{\cdot} + SX \rightarrow R_nX + S^{\cdot} .$$

The radical $S^{\cdot}$ formed interacts with the monomer M and regenerates the kinetic chain:

$$S^{\cdot} + M \rightarrow SR_1^{\cdot} .$$

The mechanism of the action of polymerisation inhibitors can be analogous, the difference consisting in the fact that the inhibitor radical cannot regenerate the chain owing to its low reactivity.

New pathways leading to the regulation of the polymerisation process have been discovered—catalysis of the reaction involving chain transfer to the monomer (CCT) and catalysis of inhibition[12–19]. As a result of the discovery of CCT, it has been possible to regulate the MW of the polymers and catalytic inhibition made it possible to regulate the rate of polymerisation.

The CCT phenomenon has been observed in the presence of cobalt complexes of porphyrins (PCo). Catalytic inhibition is manifested in the presence of model porphyrins–cobalt-phthalocyanines (PcCo).

At the present time CCT has been thoroughly investigated in relation to the polymerisation of methyl methacrylate (MMA) initiated by azobisisobutyronitrile in the presence of the tetramethyl derivative of cobalt-haematoporphyrin[12–15]. Kinetic studies showed that CCT is a highly selective process, as a result of which the catalyst hardly influences the rate of polymerisation in the concentration range 10^{-6}–10^{-4} M, regulating the MW of the polymer in accordance with the familiar Mayo equation

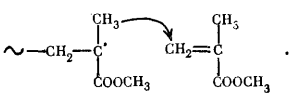
$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_{n0}} + C_n \frac{[M]}{[PCo]} ,$$

where $\bar{P}_n$ and $\bar{P}_{n0}$ are the average degrees of polymerisation in the presence and absence of the catalyst, $C_t = k_t/k_p$ is the chain transfer constant, k_t and k_p are the rate constants for chain transfer and propagation, and [M] and [PCo] are the concentrations of the monomer and the catalyst respectively.

The activity of the catalyst, estimated from the ratio of the chain transfer constants for the catalytic and non-catalytic reactions, is 10^8. The number of times each catalyst molecule is employed in the chain transfer steps reaches 10^5–10^6. Since the rate-limiting stage is the chain transfer to the metal complex and the regeneration process is fairly rapid, it was impossible to accumulate the intermediate in the catalytic reaction at concentrations sufficient for the investigation of its nature and reactivity.

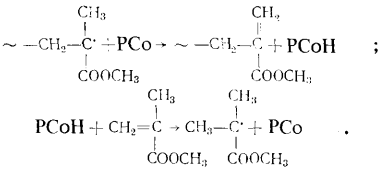
Information about the chain transfer mechanism was obtained with the aid of the NMR spectra of the oligomers[15]. Two alternative processes involving chain transfer to the monomer were analysed: via the transfer of a hydrogen atom from the radical to the monomer and via the transfer of a hydrogen atom from the monomer to the radical.

Analysis of the ratio of the intensities of the signals of the terminal and pre-terminal groups of the MMA oligomers, comparison of the average degrees of polymerisation determined from the NMR spectrum and by gel chromatography, and also analysis of the NMR spectra of the oligomers obtained from MMA deuteriated in the CH_3 group established that the chain transfer to the monomer takes place via the transfer of a hydrogen atom from the methyl group of the radical to the methylene group of the monomer:

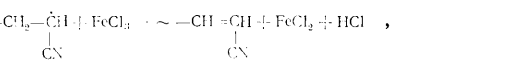


In order to explain the CCT phenomenon, the hypothesis was put forward that the active intermediate in the reaction is cobalt-porphyrin hydride. In order to demonstrate the hydride mechanism of the catalysis, the cobalt-porphyrin

hydride was synthesised[16] and in its presence MMA gave rise to an oligomer having the identical MW and structure to those of the oligomer obtained under CCT conditions. It has thus been established that the catalyst activates the polymeric radical during chain transfer and that CCT can be described by a scheme comprising concerted reactions involving the dehydrogenation of the radical and the hydrogenation of the monomer:



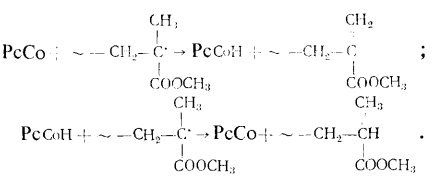
It had been known previously that the transition metal complexes interact with polymeric radicals via the oxidative abstraction mechanism[21], for example:



with rate constants in the range 10^5–10^6 litre mol^{-1} s^{-1}. Similar values of k_t, in the range (1–5) × 10^6 litre mol^{-1} s^{-1}, have been observed for cobalt-porphyrins[12]. However, one should note that only the presence of coordinated cobalt in a macroring with a specified structure constitutes the condition for the manifestation of CCT.

CCT has been observed also in the polymerisation of styrene and butyl acrylate[22,23], but in the former case its manifestation was complicated by the occurrence of side processes. In the polymerisation of butyl acrylate the rate-limiting stage is apparently the catalyst regeneration reaction and the process can therefore be regarded as reversible inhibition. One cannot rule out the possibility that the catalyst is regenerated via a mechanism involving the homolytic cleavage of the Co–C bond and not a mechanism with the dehydrogenation of the radical and subsequent transfer of the hydrogen to the monomer.

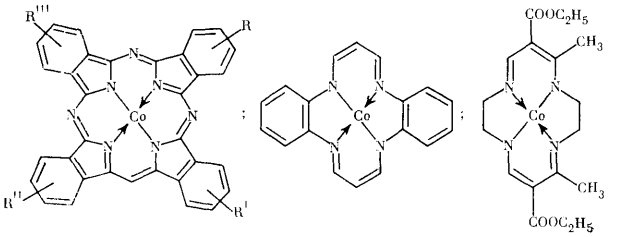
The study of the catalytic inhibition showed that the reaction proceeds via the following scheme:



The number of times each PcCo molecule is used in the course of a single polymerisation cycle is 10^2.

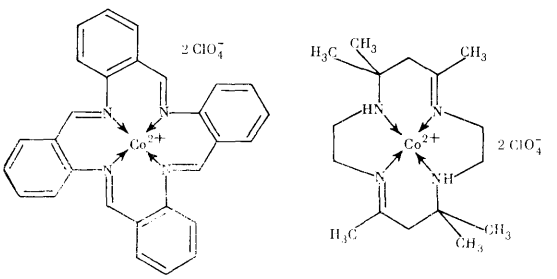
The CCT effect is manifested only when certain requirements are met by the structure of the catalyst molecule. The replacement of cobalt in the chain transfer catalyst by other metals, namely Cu, Fe, Ni, Zn, Rh, Mn, Pd, Mg, Pt, Sn, and U or by hydrogen leads to the complete loss of catalytic properties. Cobalt acetate, stearate, naphthenate, and acetylacetonate, cobalt-formazan, salcomin, and certain other cobalt complexes are inactive in the CCT to the monomer[19,23]. On the other hand, substituents in the macroring of the chain transfer catalyst do not play a decisive role in catalysis. When they are varied, the constant k_t changes within the limits of an order of magnitude[13].

It follows from the foregoing that the activity of the chain transfer catalyst is determined by the nature of the metal ion and the adjoining ligand environment and that the most important role is in this instance due to the π-electron system of the macroligand. The known chain transfer catalysts, namely the cobalt complexes of porphyrins, phthalocyanines (XXVI), tetra-azoporphyrins, and tetrabenzoporphyrins, hydroxycobalamin, and compound (XXVII), have an extensive π-conjugation system in the macroligand, which embraces almost its entire perimeter and which is quasi-aromatic in character.



(XXVI) (XXVII) (XXVIII)

Cobalt complexes with a less extensive π-electron conjugation system along the perimeter of the macroligand, namely compounds (XXVIII) and (XXX), cobalt-formazan, etc., or a non-conjugated π-electron system, namely compound (XXIX), are incapable of catalysing chain transfer.



(XXIX) (XXX)

The observed characteristics of the molecular structure of the chain transfer catalyst made it possible to carry out a specific search for new promising catalysts and to discover them. Chain transfer catalysts with $k_t \cong 10^5$–10^8 litre mol^{-1} s^{-1}, readily available for extensive industrial application, have now been obtained. The rate of chain transfer in the presence of the catalyst is 10^{10} times greater than the rate of the non-catalytic reaction and CCT under the influence of metalloporphyrins is no less efficient than enzyme catalysis.

Although porphyrin complexes can contain cobalt(III), cobalt(II), or cobalt(I), only the cobalt(II)-containing forms are active, which is consistent with the hydride mechanism of the chain transfer catalysis. The Co–H bond in cobalt-porphyrins is polarised and the hydrides of the cobalt complexes behave as weak acids[25]:

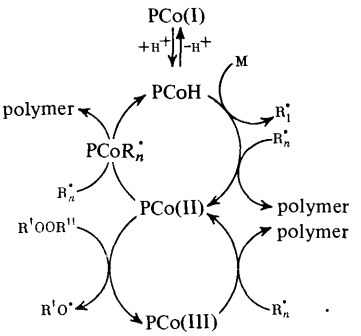


If the PCo(I) complex is fairly stable, for example, in the presence of amides, and the PCo(II) concentration in the polymerisation system is insignificant, then k_t is reduced by an order of magnitude. This is accompanied by a simultaneous increase of the rate of the catalytic chain termination reaction. Analogous effects have been observed in the presence of other porphyrin-like cobalt complexes.

Catalysts containing cobalt(III) are inactive in CCT, but under polymerisation conditions cobalt(III) is usually reduced to cobalt(II). The reduction reaction proceeds under the influence of chain propagation radicals via the oxidative chain termination mechanism[26,27] and is controlled by the axial ligand which determines the tervalent state of the cobalt atom. The addition to the polymerisation system of oxidants (benzoyl peroxide or cumenyl hydroperoxide), which selectively oxidise cobalt(II) to cobalt(III) in many catalysts,

leads to a decrease of the PCo(II) concentration and hence to a decrease of the rate of chain transfer.

The foregoing can be illustrated by the following scheme of the cyclic transformations of the catalysts in radical polymerisation:



One must note that the metal complexes investigated have many advantages compared with the familiar chain transfer agents. Thus, since the chain transfer constants in their presence are higher by 2–3 orders of magnitude than for the usual chain transfer agents, they can be introduced into the system at significantly lower concentrations in order to obtain polymers with a specified MW. The polymers thus obtained contain no fragments other than the monomer units, which is especially important in the synthesis of oligomers; on the other hand, the oligomers obtained, for example, by radical telomerisation, contain up to 15–20% of telogens, which impairs their operating properties.

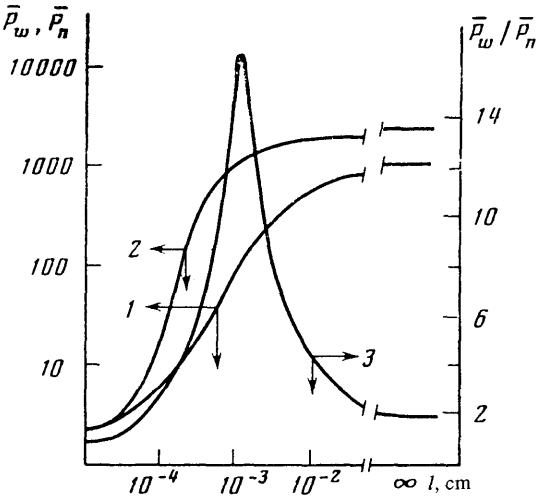
IV. KINETICS OF THE HETEROGENEOUS CATALYSIS OF CHAIN TRANSFER TO THE MONOMER

The idea of immobilising the chain transfer agent on the surface of an inert carrier in order to create catalysts capable of being regenerated was put forward immediately after the discovery of CCT.[18] Experimental and theoretical studies in recent years have now elucidated the fundamental possibilities and have led to the formulation of the main problems of heterogeneous catalysis using metalloporphyrins[8,28-30]. It has been shown that the catalytic properties of the metal complexes are not retained for all modes of addition to the surface. Thus the grafting of aetioporphyrin, attached in the *meso*-position by a single covalent bond to the "Separon" macroporous gel, leads to a catalytically active system after the introduction of cobalt. However, heterogeneous catalysts based on the *meso*-porphyrin-(II) and *meso*-porphyrin-(IX) dibasic acids have no catalytic activity. These catalysts were synthesised both by chemisorption on alumina and by grafting via amide bonds to the surface of porous glass treated with aminopropyltrichlorosilane[28].

It became evident that the covalent grafting of the metal complex onto the surface via a fairly flexible, long, and polar chain is necessary to ensure catalytic activity. This procedure was realised in the study of Pashchenko et al.[8] Subsequently the cobalt complex of tetraphenylporphyrin, which also possessed catalytic properties, was immobilised on the surface of "Separon" together with the cobalt complex of aetioporphyrin-(IX). The initial tests of the heterogeneous catalyst were carried out using the model MMA polymerisation reaction[14].

Since chain transfer in the presence of the heterogeneous catalyst takes place only on its surface, the problem arises of the role of the size of the unit cell, the reactant concentration, the viscosity of the medium, etc. in the regulation of the molecular weight distribution (MWD) in the product. The corresponding kinetic calculation of the rate of polymerisation and MWD was therefore carried out[29,30] for a model of the heterogeneous catalysis of chain transfer to the monomer. The process was modelled by the system of kinetic equations for radical polymerisation taking into account the diffusion of the reactants to the catalyst surface.

Calculations of the MWD and of the rate of polymerisation as a function of the reactant concentrations and the size and shape of the unit cell of the macroreactant explained both the common features and the fundamental kinetic differences between the CCT in the homogeneous and heterogeneous versions. In the former case the regulating factor is the volume concentration of the catalyst-chain transfer agent (PCo) and in the latter it is the linear size of the unit cell of the reactant (l).



An example of the calculated dependence of the MWD parameters and the polydispersity of the products on the linear size of the microreactor cell[44]: 1) $\bar{P}_n$; 2) $\bar{P}_w$; 3) $\bar{P}_w/\bar{P}_n$.

Whereas in the homogeneous version the polydispersity ($\bar{P}_w/\bar{P}_n$) of the product changes monotonically from 2 to 1 on increase of the catalyst concentration[17], in the heterogeneous version the polydispersity passes through a maximum as l diminishes (see Figure) and the fraction of the low-molecular-weight component of the MWD corresponding to polymerisation in a boundary layer increases. When the weight contributions of the low- and high-molecular-weight fractions are approximately the same, the maximum polydispersity of the product is observed.

In both homogeneous and heterogeneous catalysis of the chain transfer to the monomer, the overall rate of polymerisation becomes dependent on the efficiency of the transfer. The diffusion control of the disproportionation of the radicals leads to a decrease of the short chain termination constant, decreasing the rate of polymerisation.

A new geometrical factor, lowering the rate of polymerisation, appears in heterogeneous catalysis. It is the stationery gradient of the radical concentrations in the reaction cell.

The catalysis of chain transfer on the wall leads to a redistribution of the radical concentrations in space and the overall concentration of the active centres and hence the rate of polymerisation decrease at the same time. Numerical calculations for specific model variants on a computer confirmed this fully[30]. A 30% decrease of the rate of polymerisation in heterogeneous catalysis has been recorded experimentally[8], while the corresponding concentration of the cobalt complex of the porphyrin, dissolved in the monomer, did not lead to an appreciable decrease of the rate of polymerisation under analogous conditions. Experimental measurement of the rate of polymerisation in heterogeneous catalysis therefore not only constitutes a simple quantitative test of the efficiency of the catalytic properties of the surface but can also become a fundamentally new method for the investigation of the dependence of the elementary kinetic radical polymerisation constants on the length of the chain in macroradicals.

V. CATALYSIS OF OXIDATION AND HYDROXYLATION REACTIONS

It is known that metalloporphyrins catalyse the oxidation reactions of various organic and inorganic compounds. Oxygen is then coordinated to the central metal ion and one or two electrons are transferred to the oxygen with formation of superoxo- or peroxo-complexes which interact with the substrate and initiate its free-radical oxidation[31].

The processes involving superoxide complexes of porphyrins include the oxidation of adrenalin, which has been shown[32-34] to be catalysed by tetra-*p*-sulphophenylporphyrincobalt(PCo). It has been demonstrated that PCo forms a charge-transfer complex with oxygen which can dissociate to give a superoxide ion:

$$PCo + O_2 \rightleftarrows [PCo^{+}O_2^{\cdot-}] \rightleftarrows PCo + O_2^{\cdot}.$$

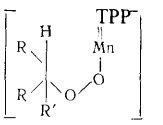
The interaction of $O_2^{\cdot}$ with adrenalin involves a complex mechanism and the first stable product is adrenochrome. The system described is highly effective in an aqueous medium at biologically important pH and each catalyst molecule participates in at least 100 oxidation steps.

The oxidation reactions initiated by superoxide proceed via a radical-chain mechanism with formation of a large set of products[32]. In the presence of an excess of the reductant, metalloporphyrins can catalyse also non-chain oxidation which is both regioselective and stereoselective. Thus the oxidation of olefins by molecular oxygen takes place extremely effectively in the presence of the manganese complex of *p*-methoxytetraphenylporphyrin (TPPMnCl) and an excess of sodium tetrahydroborate. This system models the action of mono-oxygenating enzymes, the haem prosthetic group of which incorporates metalloporphyrins in most cases. In living organisms monoxygenases catalyse the processes involving the incomplete incorporation of oxygen. One of the components of hydroxylase systems, cytochrome P-450, initiates the hydroxylation and epoxidation of steroid and aliphatic olefins, aliphatic acids, and alkanes. A characteristic feature of the action of hydroxylases is that the oxidation is by molecular oxygen and the presence of a reductant is necessary for the functioning of the system.

It is known that the porphyrin complexes of manganese(II), obtained by the reduction of manganese(III), activate molecular oxygen and catalyse the oxidation of various olefins[35-37]. This model hydroxylase system contains an excess of reductant, is insensitive to the action of radical inhibitors, and a set of products uncharacteristic of radical oxidation is formed in its presence. Saturated alcohols and ketones have been detected among the olefin oxidation products.

The oxidation of aliphatic (ethylene, propene, hex-1-ene, hex-2-ene) and steroid (androstene and cholesterol) olefins has been investigated at room temperature in dimethylformamide and a 1:1 benzene–ethanol mixture by molecular oxygen in the presence of the TPPMnCl–$NaBH_4$ system and it has been shown that mono- and di-substituted olefins are oxidised with formation of a mixture of ketones and alcohols[38,39]. Ketones and secondary alcohols are formed from asymmetrically substituted olefins (propene and hex-2-ene), i.e. the process is regioselective. The rate of oxidation of olefins depends on the substituent at the carbon atom involved in the double bond and varies in the sequence ethylene < propene < hex-1-ene < hex-2-ene. Tri-substituted steroid olefins are oxidised regioselectively and stereoselectively at a higher rate and with nearly 100% conversion, forming only 5α-substituted alcohols.

The formation of tertiary alcohols from trisubstituted olefins and of ketones and secondary alcohols from mono- and di-substituted olefins apparently proceeds via the same mechanism involving the reduction of TPPMnCl to a manganese(II) complex of TPP as the first stage with subsequent formation of a complex with molecular oxygen: TPP = Mn^{+}–O_2. In this complex manganese(II) and O_2 are located to one side of the plane of the porphyrin ring[40] and the electrophilic addition of the complex to the double bond of the olefin leads to the formation of a cyclic intermediate complex analogous to complexes involving monoxygenases[41]:



The reductive cleavage of the C–Mn bond by $NaBH_4$ leads to an intermediate product of the peroxide type, the mode of the subsequent cleavage of which depends on the structure of the substituents R and R' at the double bond. The formation of ternary metalloporphyrins–oxygen–olefin complexes has been observed experimentally[42]. Within the framework of the mechanism involving the formation of complexes of this type, it has been possible to formulate a kinetic scheme for the oxidation of olefins and to calculate the constants for the individual stages[43].

The effective charge of the metal ion and hence the degree of polarisation of the reactants in the formation of their complexes with the catalyst may be influenced by the presence of extraneous ions in solution. The introduction of neutral salts into the O_2 + TPPMnCl + $NaBH_4$ system inhibits the oxidation of cholesterol and the magnitude of the effect depends on the nature of the salt and the solvent.

As already mentioned, the catalytic system described above exhibits certain properties characteristic of monoxygenases: a non-radical character and hence the selectivity of the process catalysed, which proceeds via the formation of a cyclic intermediate complex, a high specificity of action, and inhibition by neutral salts. By altering the nature of the reducing agent, it is probably possible to change the direction of the process, obtaining, for example, epoxides as the primary

products, and, by altering the nature of the substrate, it is possible to achieve a higher affinity of the latter for the catalyst and hence a higher rate of oxidation.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 236-250 (1984) U.D.C. 541.427;547.514,72;539.383

The Polymerisation of Solid Monomers Under Conditions of Deformation at a High Pressure

A.A.Zharov

The polymerisation of solid monomers deformed under high pressure has been examined. The anomalously high reactivity of the substances under these conditions, and the reasons for it, have been discussed. The possibilities provided by the methods of formal kinetics for the description and study of the mechanism of polymerisation have been demonstrated for the polymerisation of acrylamide.
The bibliography contains 56 references.

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I. INTRODUCTION

The formation of macromolecular compounds with shear deformation of the solid monomers under a high pressure was first detected by Enikolopov, Zharov, and Kapustyan in 1964.

In the first studies[1], for ten monomers of different character, it was shown that shear deformation and high pressures (SD + HP) are powerful factors stimulating the polymerisation of solid monomers. In a short time, studies in this field have extended and have led to considerable progress in the investigation of the reactivity of solid monomers and the regular features of polymerisation under SD + HP conditions. Compounds of various classes have now been studied: alkene derivatives, compounds of the acetylene series, nitriles, heterocyclic compounds, aromatic hydrocarbons, etc., corresponding to more than one hundred individual substances. Most of these substances can form macromolecular compounds under SD + HP conditions[1-25]. The study of the polymerisation has revealed unusual features in the chemical processes, for example the anomalously high reaction rates and the dependence of the kinetics of polymerisation on the magnitude of the shear deformation.

About one hundred papers have been published on the formation of polymers under SD + HP conditions. Most of the work in this field has been carried out by Soviet scientists. In recent years, a number of studies in this area have been carried out by the Japanese workers Ogo and Okuri[11,12,16].

II. CHARACTERISTIC FEATURES OF THE TRANSFORMATIONS AND REACTIVITY OF ORGANIC COMPOUNDS DEFORMED AT HIGH PRESSURES

Experiments under SD + HP conditions are carried out on an apparatus of the anvil type[26-28], whose operational principles were first realised by Bridgman, and which is based on the fact that the compression of a solid specimen between two plates does not lead to flow of the substance if a sufficiently thin specimen is taken. A version of this apparatus is given in Fig.1. The solid reaction mixture is placed between the anvils, which are made of ball-bearing steel or VK-6 hard alloy and which have the form of truncated cones. The thickness of the specimen depends on the nature of the substance and the area of the working surface of the anvils; for an anvil area of 1 cm^2, the weight of the original specimen is 5–10 mg. The anvils are compressed by means of a press capable of creating a load of up to 100 tons; a pressure of up to 10 GPa is produced in the specimen. After the pressure has been established, the specimen is deformed by rotating the lower anvil, which is on a platform placed on a supporting ball bearing. The platform is rotated by an electric motor and reducing gear. The shear forces are measured using an assembly consisting of a spring element, levers, and a mechanotron, the signal from which is passed to a recorder. The anvils can be kept at a constant temperature in the range 77–500 K.

Experiments have shown[1-25] that under SD + HP conditions, polymers can be formed by organic compounds of various classes: a) compounds with one $-C{=}C-$ bond: hydrocarbons (ethylene, styrene, α-methylstyrene, etc.), esters (alkyl acrylates, alkyl methacrylates), acids (acrylic, methacrylic, crotonic, etc.)[1,7], anhydrides[6], amides, imides[5], and nitriles[17,20], chloro-compounds (dichloro- and trichloropropenes, etc.)[15]; b) compounds with conjugated double bonds: butadiene, cyclopentadiene[7,14], 1,1,2-trichlorobutadiene[15], etc.; c) compounds with a triple bond: derivatives of acetylene (*p*-diethynylbenzene, tolan[1], derivatives of diacetylene[16], etc.), nitriles (malononitrile, cyanacetamide, terephthalodinitrile, 4-cyanopyridine, etc.)[17-19]; d) heterocyclic compounds: trioxan, hexamethyltrisiloxane[1,7], thiophene, pyridine[20,21]; e) aromatic compounds: benzene[25], napthalene, anthracene, phenanthrene[19,20,22], quinones, etc.[23,24]

The study of a large number of organic compounds indicates that if the molecules of a substance contain the groups $-C{\equiv}C-$, $-C{=}C-$, $-C{=}N-$, heterocyclic rings, or aromatic rings, then the conditions produced when the specimen is deformed can induce the formation of macromolecular compounds. Compounds with different reactivities can react: monomers which readily form polymers by different mechanisms in both the liquid and solid phases (acrylamide, styrene, etc.[1,30]); compounds which in other conditions do not give macromolecular products in the solid state (methyl methacrylate[8], maleic anhydride[1,6]); and substances which polymerise with difficulty (nitriles[20], derivatives of acetylene[1,7], whose polymerisation takes place only under severe conditions at high temperatures.

Parallel transformations in addition to the main reaction are often observed under SD + HP conditions. Polymerisation may be accompanied by Diels–Alder reactions[14], and the substances may react with atmospheric oxygen and moisture at the moment of deformation. If the compound contains two or more functional groups capable of reacting under SD + HP conditions, cross-linked insoluble polymers are formed[14,15,18,29]. The influence of side reactions can be decreased by selecting a range of pressures at which polymerisation takes place without complications; the products are analogous to the polymers synthesised under ordinary conditions. Styrene, methyl methacrylate, and trichlorobutadiene are converted into polymers which have the same structures as the corresponding polymers obtained by radical polymerisation[8,15,30]. Trioxan forms a polymer whose infrared spectrum is identical to that of polyoxymethylene obtained by radiation polymerisation[7]. Derivatives of maleimide give polymers corresponding to those obtained by radiation polymerisation[5].

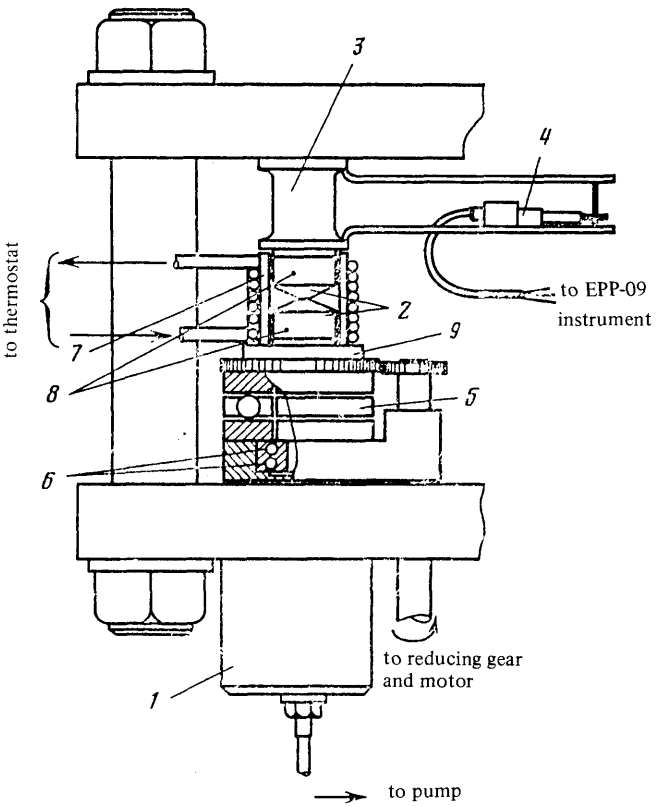


Figure 1. Apparatus for studying the transformations of substances under SD + HP conditions[28]: *1*) cylinder of hydraulic press; *2*) anvils; *3*) spring element; *4*) mechanotron; *5*) supporting ball bearing; *6*) radial ball bearing; *7*) constant-temperature jacket; *8*) positions for thermocouples; *9*) step bearing of heat insulator.

The reactivity of compounds under SD + HP conditions is such that high degrees of transformation are achieved in anvil rotation times measured in seconds[3,4,7]; the deformation of the solid specimen is a necessary condition for the chemical reaction. Treatment of the reaction mixture at the same pressures for times which are 10^2–10^3 times the duration of the experiments under SD + HP conditions does not lead to any significant transformation[1,7].

A general feature of chemical processes under SD + HP conditions is that the extent of the transformation depends on the magnitude of the shear deformation (usually expressed in terms of the angle of rotation of the anvil). The nature of the curves giving the dependence of the degree of conversion on the angle of rotation may vary, but the conversion always increases with increase in the deformation (Fig.2). The yield of reaction products increases with increase in pressure. With decrease in temperature, the rate of transformation decreases; the temperature coefficient of the reaction is small, however, and polymerisation can take place even at liquid-nitrogen temperature (acrylamide, butadiene, etc.)[6,7,14,31].

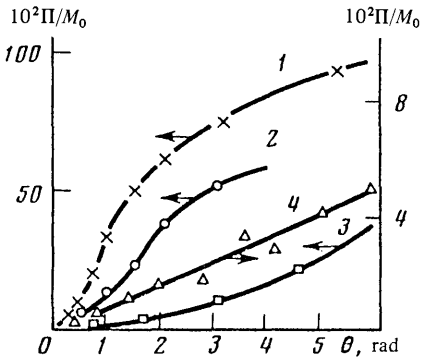


Figure 2. Dependence of the yield of polymer (Π/M_0) on the angle of rotation (θ) of the anvils (2000 MPa, 293 K)[7]: *1*) acrylamide, *2*) methacrylamide, *3*) maleic anhydride, *4*) trioxan (1000 MPa).

Other characteristic features of the formation of macromolecular compounds under SD + HP conditions are conveniently considered for specific examples.

1) *Acrylamide.* This monomer polymerises readily under SD + HP conditions, beginning at a pressure of several hundred MPa[4,6,31,32]. The study of the transformations of this monomer has resolved the question of when polymerisation takes place: whether the polymer is formed at the moment of deformation, or whether the growth of the polymer chains takes place after the SD + HP experiment is complete, as a result of the initiation of active centres, accumulated in the substance during its deformation. Which of these possibilities is realised was established[32] by measuring the shear stress of the specimen during deformation. Fig.3 gives the observed dependence of the shear stress (τ) on the angle of rotation of the anvil (θ) and on the quantity of polymer formed in the specimen (Π/M_0). The curves in Fig.3 show the accumulation of polymer in the specimen at the moment of deformation. Moreover, according to the results of the same study[32], for the mixture of acrylamide and polyacrylamide prepared by mechanical mixing or partial polymerisation, the values of τ correspond to the dependence of Π/M_0 given in Fig.3*b*. Thus polymerisation takes place at the moment of deformation of acrylamide, and the contribution of post-polymerisation is insignificant or non-existent.

2) *Styrene*[30]. The structure of the polymer obtained by the deformation of solid styrene at a pressure of 1000 MPa is extremely close to that of the polymer synthesised by radical polymerisation. With increase in pressure, however, the structure of the polymer formed under SD + HP conditions changes: there is a decrease in the proportion of units in the regular, predominantly syndiotactic, groups characteristic of ordinary polystyrene, and an increase in the proportion of units in short and irregular blocks. This phenomenon may be related to "head to head" connection or chain branching, and may be the consequence of the rupture of benzene rings. Side reactions taking place in parallel at pressures above 4000 MPa give a product made up of short polystyrene blocks, which are joined to one another by groups with an irregular structure.

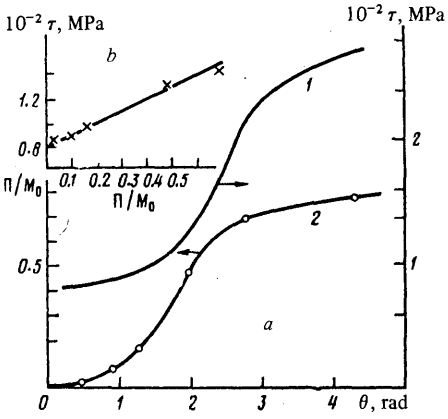


Figure 3. Relationship between the shear stress of the specimen τ, the degree of transformation Π/M_0, and the angle of rotation of the anvils θ;[32] *a*) dependence of the shear stress and the degree of transformation on the angle of rotation; *b*) dependence of the shear stress on the concentration of polymer in the specimen.

Thus with increase in pressure in SD + HP experiments there may be a change in the structure of the resultant macromolecular compound as a result of side reactions which are not revealed at low pressures.

3) *Trioxan*. The study of the polymerisation of trioxan has shown[7] that this monomer is polymerised with great difficulty under SD + HP conditions. At pressures of 3000–4000 MPa and θ = 4–5 rad, the yield of polymer did not exceed 1%. At lower pressures (1000–1500 MPa), no polymer was detected. If however trioxan is treated beforehand with ionising radiation, that is if ionic active centres are introduced, then this monomer polymerises readily on deformation even at a pressure of 1000 MPa to give polyoxymethylene (see Fig. 2).

The formation of polyoxymethylene under SD + HP conditions from trioxan containing ionic active centres indicates that the formation of the macromolecules is not due only to the production of the active centres and that it is the deformation of the solid monomer than ensures the necessary conditions for the chain process of growth of the polymer molecules.

Compounds whose polymerisation is difficult or not detected at all under ordinary conditions are of particular interest.

1. Polymerisation of Nitriles and Aromatic Compounds

Nitriles under ordinary conditions undergo poly-addition either under the influence of large doses of ionising radiation or in the presence of Lewis acids with cocatalysts. The passivity of the cyano-group with respect to polymerisation is explained by the fact that the formation of sequences of $-C=N-$ bonds in many cases is a thermodynamically unfavourable process[33].

Under SD + HP conditions, however, solid nitriles can react to form sequences of $-C=N-$ bonds; the polymers obtained are brown or black, and give an EPR signal in the form of the singlet characteristic of polyconjugated systems[19]. The change in the colour of the nitriles on polymerisation made it possible to use a micro-apparatus with transparent diamond anvils to follow visually the transformations of the nitriles during deformation[18]. These observations, made for tetracyanoethylene, malononitrile, and terephthalodinitrile, made it possible to record the breakdown of the crystalline blocks in the field of the shear stresses, to observe the displacement zones in the substance, and, which is most important, to detect the development of the polymerisation process as the deformation of the specimen increased[18].

The transformations of other nitriles under SD + HP conditions was studied using ordinary apparatus[17–20]. The reactivity of these compounds varies over a wide range[7,18]. The least reactive are derivatives of compounds of the aliphatic series: stearonitrile and palmitonitrile do not react even at 10000 MPa; succinonitrile is polymerised at this pressure, but at higher values of the deformation. Increase in the number of CN groups in the molecule, and additional functional groups such as $-C=C-$, NO_2, aromatic rings, etc. increase the reactivity of a compound to a considerable extent: benzonitrile reacts at 8000 MPa, *p*-nitrobenzonitrile at 5500 MPa, fumaronitrile at 3000 MPa, malononitrile at 1000 MPa, etc.[18] Under deformation conditions, both functional groups often react. Thus 4-cyanopyridine and benzonitrile react both at the $C\equiv N$ group and with opening of the aromatic ring. If the molecule contains a group more reactive than CN, for example the $-C=C-$ group in acrylonitrile, the polymerisation takes place primarily through this group[20].

Thus the transformations of nitriles are accompanied by the formation of products with a high molecular mass. The production of the structure of the polymeric molecules in the general case, however, is due not only to the successive attachment of CN groups to one another but also to the reaction of other functional groups ($-C=C-$, amide, NO_2, etc.)[18].

Aromatic hydrocarbons under SD + HP conditions undergo unusual transformations, whose chief characteristic is the opening of the aromatic rings[4]. It is known that aromatic fragments of molecules are among the most stable in chemical reactions. Very high pressures of tens of thousands of MPa generally do not bring about the transformation of aromatic hydrocarbons[34].

Benzene, pyridine, and thiophene are classical examples of aromatic compounds. All these substances at 8000–10000 MPa under shear deformation conditions undergo transformations accompanied by rupture of the aromatic ring and the formation of macromolecular compounds[9,20,35,36]. For example, benzene is converted into a brown polymer which does not melt and which is insoluble in common solvents; the infrared spectrum of the product does not contain absorption bands characteristic of aromatic derivatives, and is identical to the spectrum of the polyacetylene obtained on Ziegler–Natta catalysts, that is under SD + HP conditions, benzene is converted into a polymer made up of sequences of $-C=C-$ bonds[25,36]. The formation of polyene structures under SD + HP conditions is unique. The opening of the benzene rings under other conditions has been reported; it can take

place, for example, under the influence of radiation[37], ultrasonic waves[38], and shock waves[39], but the formation of sequences of −C=C− bonds is not observed.

Polynuclear compounds with isolated or condensed rings (naphthalene, biphenyl, anthracene, phenanthrene, etc.) under SD + HP conditions also form macromolecular compounds by rupture of the aromatic ring[20,36]. As with nitriles, the pressures at which aromatic compounds begin to react are characteristic of each substance[7]. Thus anthracene begins to polymerise at a pressure of 2000 MPa and above, naphthalene at 4000 MPa, biphenyl at 8000 MPa, and bibenzyl at 2,3-dimethylnaphthalene at 10000 MPa (durene does not react at these pressures[36]).

The reactivity of hydrocarbons under SD + HP conditions depends on the number of aromatic rings in the molecule, on the way in which they are connected, and on the nature of the substituents[35,36]. The stability of an aromatic derivative decreases with increase in the number of rings (benzene is more stable than naphthalene, naphthalene is more stable than anthracene, and biphenyl is more stable than terphenyl). For a given number of rings, the reactivity of the hydrocarbons depends on the way in which the rings are connected; anthracene reacts at lower pressures than phenanthrene, and phenanthrene reacts before terphenyl. Compounds with isolated rings are more stable than those with condensed rings: biphenyl is more stable than naphthalene, etc. The reactivity is influenced strongly by aliphatic groups. Dimethylnaphthalene, bibenzyl, and durene are much more stable in SD + HP conditions than their non-substituted analogues. The stability of these compounds in a field of mechanical stresses cannot be explained within the framework of the usual concepts of organic chemistry, since CH_3 or CH_2 groups have practically no influence on the stability of an aromatic ring. It has been suggested[7,35] that mechanical stresses may be "concentrated" in chemical bonds in different ways; mobile aliphatic groups prevent the "concentration" of the mechanical stresses in the molecule or its fragments, leading to a decrease in the reactivity of the substances under SD + HP conditions.

2. Estimation of the Rate Constants of Polymer Chain Growth

Chemical reactions under SD + HP conditions take place in times measured in seconds or fractions of a second, that is the reaction rates are very high. In a number of cases it has been possible to estimate the lower limit of the reaction rate constant[7,42].

Table 1. Rate constants for the growth of polymer chains (mole litre^{-1} s^{-1}) calculated for the liquid phase and observed for DS + HP.

Monomer	p, MPa	T, K	t, s	P	k_p (calc.)	k_p (SD + HP)	Refs.
Styrene	1000	195	1	1000	1.6	$\geqslant 10^2$	[7, 30]
Acrylamide	1000	150	1	1000	1.5	$\geqslant 10^2$	[3, 7]
Butadiene	2000	150	1	200	10^{-3}	$\geqslant 20$	[7, 29]

The lower limit of the rate constant is calculated using the obvious inequality[7]:

$$k_p \geqslant P/M_0 t$$

relating the rate constant of the propagation of the polymer chains (k_p, litre mole^{-1} s^{-1}) to the concentration of monomer (M_0, M), the degree of polymerisation (P), and the reaction time (t, s). By substituting the experiment time and the degree of polymerisation in the inequality obtained, it is possible to calculate the lower limit of the rate constant of polymer chain propagation. These estimates have been carried out for various polymerisation reactions (Table 1). The examples given in Table 1 indicate that under SD + HP conditions, the polymerisation rate constants are greater by 2–5 orders of magnitude than the corresponding rate constants for polymerisation in the liquid phase. In other words, on deformation of the solid monomers the reaction of the double bonds with the radicals is stimulated.

Table 2. Degree of transformation, yields of product, and rate constants for the dimerisation and trimerisation of cyclopentadiene[42].

T, K	p, MPa	t, h	$10^2 M/M_0$	$10^2 2M_2/M_0$	$10^2 3M_3/M_0$	k_d, litre mole^{-1}s^{-1}	k_t/k_d
Experiments in the liquid phase*							
353	500	1	8.35	91.3	0.32	$2.4\cdot10^{-3}$	$1.5\cdot10^{-3}$
353	0.1	5	31.7	68.2	0.076	$9.0\cdot10^{-5}$	$1.05\cdot10^{-3}$
293	0.1	170	56.9	43.1	0.0021	$7.2\cdot10^{-7}$	$6.7\cdot10^{-1}$
Experiments under SD + HP conditions**							
153	4000	0.02***	45.5	47.3	7.2	—	$2.5\cdot10^{-1}$

* 10% solution in toluene used.
** Pure cyclopentadiene.
*** Angle of rotation of anvils equal to 2.6 rad.

The reaction rate constants under SD + HP conditions were also estimated quantitatively in a study of the dimerisation of cyclopentadiene[42]. In the liquid phase this reaction is accompanied by the formation of small quantities of oligomers, mainly trimers, so that the kinetics of dimerisation are described by equations which take account of the formation of the trimers[29,42]:

$$-\frac{dM_1}{dt} = \frac{1}{2}\frac{dM_2}{dt} = k_d M_1^3 \quad , \tag{1}$$

$$\frac{dM_3}{dt} = k_t M_1 M_2 \tag{2}$$

where M_1, M_2, M_3 are the concentrations of the monomer, dimer, and trimer, M; and k_d and k_t are the dimerisation and trimerisation constants respectively. Some of the experimental results, and also the constants k_d and k_t calculated using the equations obtained by solving the differential equations (1) and (2)[7,29], are given in Table 2. When the reaction is carried out under SD + HP conditions, the trimerisation rate constant increases considerably relative to the dimerisation rate constant. Comparison of the dimerisation rate constants calculated for the liquid phase and observed under SD + HP conditions gives an interesting result. k_d for the liquid-phase reaction (at the temperature and pressure of the SD + HP experiment) was calculated from the known values of the activation energy[40] and the volume effect of the formation of the activated complex[41]. The calculated rate was 2×10^{-9} mass % min^{-1}, whereas the rate observed under SD + HP conditions is not less than 15–20 mass % min^{-1}, that is it is 10^{10} times greater[42].

Thus the estimates of the reaction rate constants under SD + HP conditions indicate that the substances show an anomalously high reactivity under conditions of deformation in the compressed state.

3. The Role of Heat Production Under SD + HP Conditions

The deformation of solid specimens involves considerable mechanical work, most of which is converted into heat; the solution of the problems related to the estimation of the heat production in a substance is therefore important for the interpretation of the results of SD + HP experiments, and in particular for the determination of the factors responsible for the high reactivity. Calculations and direct measurements of the temperature of specimens have shown[7,49] that the total heat production in a substance on deformation in an apparatus of the anvil type is slight, and cannot be responsible for the high rate of the chemical transformations.

Another mechanism which can be introduced to explain the high reactivity of the compounds is based on the concept of "hot spots". It is suggested[7] that at the moment of deformation in the specimen there exist zones in which there is a sharp increase in temperature as a consequence of the non-uniformity of the specimen, the separation of the plastic flow of the substance, or other factors. The size of these zones is obviously greater by many orders of magnitude than that of the molecules, and the temperature in these "hot spots" cannot exceed the melting point of the substance at the given pressure[44].

To resolve the question of the existence of these molten zones under SD + HP conditions and their role as places where the reactions take place, a study was made of the influence of pressure on the rate constants of the iso- and syndiotactic addition of the growing polymer radical to the double bond of methyl methacrylate (k_i and k_s) in the liquid-phase polymerisation[45] and the polymerisation of this monomer under SD + HP conditions[8]. The difference in the volume effects of activation $\delta\Delta V^{\neq} = \Delta V_i^{\neq} - \Delta V_s^{\neq} = -0.3$ cm^3 mole^{-1} (liquid-phase polymerisation, pressure range 8000–1050 MPa) and the difference in the activation energy $E_i - E_s$, which was found to be 1.1 kcal mole^{-1} at both ordinary and high pressures, were determined. For SD + HP conditions, it was found that $\delta\Delta V^{\neq} = -0.08$ cm^3 mole^{-1}.[8] The values of $\delta\Delta V^{\neq}$ and $E_i - E_s$ obtained were used to verify the concept of "hot spots".

If the reaction takes place in the zones of the molten monomer, the change in lg (k_i/k_s) with change in pressure under SD + HP conditions should be determined by the quantity $|\delta\Delta V^{\neq}| > 0.3$ cm^3 mole^{-1}, since increase in pressure is accompanied by an increase in the temperature of the molten zones as a result of the increase in the melting point with increase in pressure. Thus the value $\delta\Delta V^{\neq} = -0.08$ cm^3 mole^{-1} found under SD + HP conditions does not agree with the suggestion that molten zones exist.

The applicability of the concept of "hot spots" can also be verified by another method, by comparing the values of k_i/k_s. This ratio is appreciably higher under SD + HP conditions than for polymerisation in the liquid phase[7]. To explain this difference, it is necessary to assume that the heat production in the monomer on deformation takes place up to a temperature ~ 100 K higher than the melting point of methyl methacrylate at the given pressure, but this contradicts existing ideas about local heat production[44]. Thus under SD + HP conditions, either no local molten zones of monomer are produced, or this phenomenon does not make a significant contribution to the chemical process.

4. Copolymerisation Reactions

A number of studies have been carried out for reaction mixtures consisting of two monomers[46–49]. When specimens of mixtures of acrylamide and methacrylamide with the eutectic composition (87% acrylamide and 13% methacrylamide) were deformed, a reaction was observed, accompanied by the formation of polymeric products (pressure range 500–1500 MPa, temperature 293 K). Gel-permeation chromatography indicated that copolymers are formed[46]. An interesting feature is that the rate of the copolymerisation of acrylamide and methacrylamide is greater than the rates of polymerisation of pure acrylamide and methacrylamide.

The study of the copolymerisation of mixtures of maleic anhydride and acenaphthene under SD + HP conditions[47,49] showed that the nature of the dependence of the composition of the copolymer on the composition of the original mixture is the same as that for the liquid-phase copolymerisation of the same monomers in acetone solution. The composition of the copolymer remains unchanged with change in the composition of the original mixture (with increase in the proportion of maleic anhydride from 20% to 85%). This was attributed[47] to the reaction of maleic anhydride and acenaphthene to form a charge-transfer complex, which polymerises rapidly and forms a copolymer of definite composition.

Copolymerisation reactions are often sensitive to both the mechanism of polymerisation and the phase state of the original mixture of the monomers. These reactions include the copolymerisation of styrene and methyl methacrylate, so that this reaction has been studied in detail under SD + HP conditions[6,48,49]. The experiments were carried out at 2000 MPa, 195 K, and angles of rotation of the anvils to give a yield of copolymer not exceeding 10%. Studies of the infrared and NMR spectra of copolymers of styrene and methyl methacrylate (obtained under SD + HP conditions, in the liquid phase, and with radiation-initiated polymerisation of the solid monomers), fractionation of the polymeric products, and subsequent analysis of the fractions gave the following results[48]: 1) under SD + HP conditions, mixtures of styrene and methyl methacrylate react to give copolymers; 2) the nature of the distribution of the units of styrene and methyl methacrylate is the same for the copolymer macromolecules obtained by radical copolymerisation and the copolymers obtained under SD + HP conditions; 3) the copolymers obtained by solid-phase polymerisation show a distribution of the units approaching that found for a mixture of homopolymers of styrene and methyl methacrylate; 4) the dependence of the yield of copolymer on the composition of the original mixture, obtained under SD + HP conditions, is close to that for the liquid-phase copolymerisation (the form of this dependence is quite different for the solid-phase copolymerisation).

Thus in spite of the fact that the original solid mixtures of monomers are non-uniform, their deformation is accompanied by effective mixing of the components and the formation of copolymers with uniform compositions. Moreover, the composition of the copolymers and the distribution of the monomeric units in the polymer chain are close to those which are observed in the copolymers obtained by liquid-phase radical polymerisation. From these factors, it was concluded[48] that the state of a substance under SD + HP conditions, according to a number of its properties, is close to the liquid state (a quasi-liquid state).

III. KINETICS AND MECHANISM OF POLYMERISATION UNDER CONDITIONS OF SHEAR DEFORMATION AND HIGH PRESSURES

To determine the mechanism and characteristic features of the kinetics of polymerisation reactions with SD + HP, a series of investigations was carried out, involving the detailed study of the polymerisation of acrylamide, and including studies of the physical state of the substance

during its deformation[50-52,54] and a series of kinetic measurements and calculations undertaken to investigate the mechanism of polymerisation[3,32] and to find the rate constants of the elementary stages of the polymerisation of acrylamide[7,53,55].

These studies established a number of general regular features of polymerisation under SD + HP conditions. It was found that the yield of polymer at constant pressure and temperature depends on the magnitude of the deformation and is independent of the rate of deformation of the specimen[3,7]. The kinetic curves are *S*-shaped (Fig.4), and the point of inflection corresponds to the range in which there is a change from internal displacement of the layers of substance to the surface slip of the anvils over the specimen[7]. It can be seen from Fig.4 that with increase in pressure, the position of the point of inflection is displaced to the range of higher degrees of conversion, due to the increase in the strength of the adhesion of the specimen to the material of the anvils. The calculations were carried out using data relating to the range in which the angle of rotation of the anvils corresponded to the magnitude of the deformation of acrylamide[7]. The molecular mass of polyacrylamide at first increases with increase in the deformation, reaches a maximum for 2–8% conversion (depending on the conditions of the experiment), and then decreases (Fig.5).

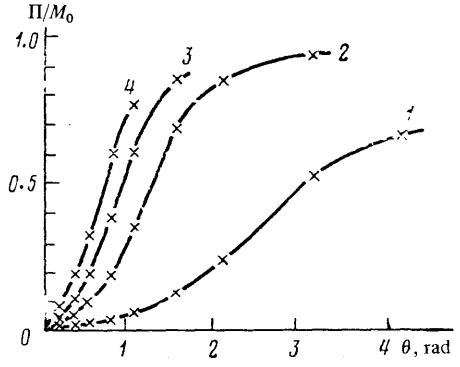


Figure 4. Dependence of the yield of polyacrylamide on the angle of rotation of the anvils at 293 K and different pressures[7]: *1*) 1000, *2*) 2000, *3*) 2500, *4*) 3000 MPa.

A study of the kinetics of the dependence of the polymerisation of acrylamide on the radical acceptors added to the monomer and experiments with previously irradiated specimens (treatment with γ-rays from a ^{60}Co source)[32] indicated that the polymerisation of acrylamide takes place by a radical mechanism. The increase in the rate of polymerisation is proportional to the increase in the concentration of polymer in the specimen[32]. The mechanism of the increase in the rate of polymerisation with increase in the concentration of the polymer is not clear. The appearance of polymer leads to an increase in the shear stress applied to the specimen (see for example Fig.3a), and this may lead to an increase in the reaction rate, since the shear stress applied to the reaction mixture under SD + HP conditions influences the rate of the chemical process[56]. It is also extremely probable that the appearance of polymer molecules in the specimen facilitates the production of regions in which the mechanical stresses leading to the generation of active centres for polymerisation are concentrated[32].

On the basis of the regular features observed, a mechanism was proposed for the polymerisation of acrylamide[7,53,55]; the following assumptions were made: a) all the elementary stages of polymerisation (initiation, propagation, and bimolecular termination of the chain) take place during the deformation of the specimen; the collision of the reagent molecules takes place only as a result of the movement of the layers of the substance relative to one another on shear deformation. Thus the independent variable in the equations describing the elementary stages should be not time but the magnitude of the deformation of the substance; b) the production of active centres (radicals) takes place mechanochemically in a medium of the monomer in regions where mechanical stresses are concentrated, and the number of such regions is proportional to the quantity of polymer formed. The differential equations are written as follows[53]:

$$\frac{dR}{dx} = k_i' M_0 + k_i \Pi - k_t R^2 \qquad (3)$$

$$-\frac{dM}{dx} = \frac{d\Pi}{dx} = k_p M_0 R \qquad (4)$$

where x is the magnitude of the shear deformation ($x = r\theta/z$); r the radius of the differential zone of the specimen, cm; θ the angle of rotation of the anvil, rad; z the height of the specimen, cm; M, Π, and R the concentrations of the monomer, polymer, and radicals, M; k_i' and k_i the rate constants of the initiation in the pure monomer and in the presence of polymer; and k_p and k_t the rate constants of the propagation and termination of the polymer chains.

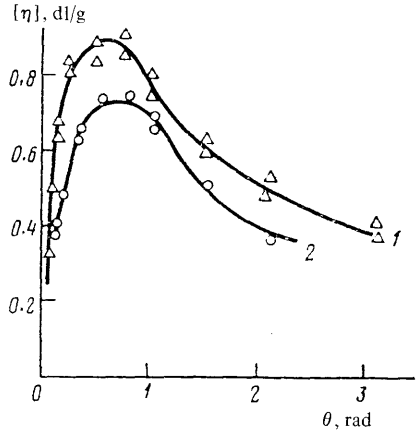


Figure 5. Dependence of the characteristic viscosity [η] of polyacrylamide on the angle of rotation of the anvils at 293 K[7]: *1*) 1000, *2*) 2000 MPa.

Solution of Eqns.(3) and (4) using the principle of stationary character gives the expression[7,53]:

$$\frac{\bar{\Pi}}{M_0} = \frac{k_p^2 k_i}{8k_t} M_0 \frac{(r_2^2 + r_1^2)}{z^2} \theta^2 \qquad (5)$$

where $\bar{\Pi}$ is the average concentration of the polymer in the annular zone of the specimen bounded by the radii r_1 and r_2.

Fig.6 gives the dependence on θ obtained at different pressures for different radial zones of the specimen. The experimental data obtained lie effectively on straight lines on these coordinates.

Eqn.(5) has been used[53] to verify the dependence of the yield of polymer on the radius of the anvil. Fig.7 gives the dependence of $(\Pi/M)^{1/2}$ on θ, obtained by averaging the results of 16 experimental series for anvils with diameters of 10 mm and 20 mm. The slopes of the straight lines corresponding to experiments with anvils of different diameter differ by a factor of two, and the yields of polymer differ accordingly by a factor of four. According to Eqn.(5), the yields of polymer for a fixed angle of rotation and the same specimen thickness should also differ by a factor of four; thus these results indicate good agreement between theory and experiment.

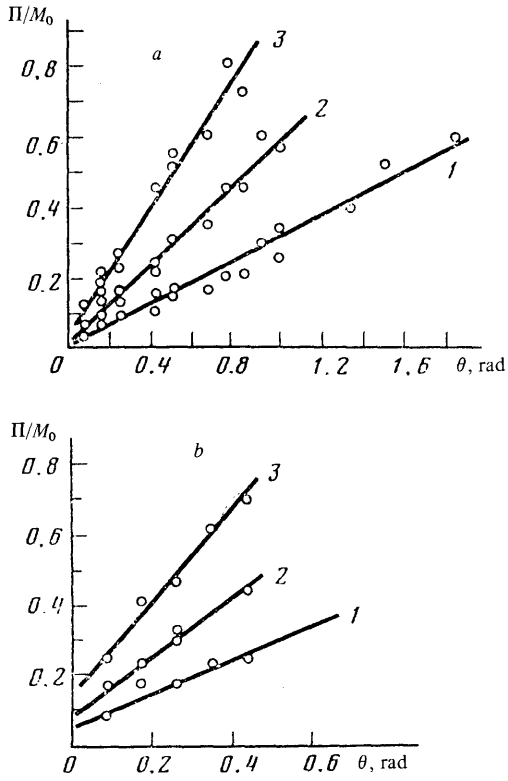


Figure 6. Dependence of (Π/M_0) on θ, obtained for different zones of the specimen at different pressures[53]: *a*) 1000, *b*) 3000 MPa; *1, 2, 3*) radial zones of specimens with diameters from 0 to 10 mm, from 10 mm to 15 mm, and from 15 mm to 20 mm respectively.

In the work cited[53], the experimental data on the molecular masses were treated using an equation relating the mean-molecular mass of the resulting polymer M_m to the angle of rotation of the anvils θ. The degree of polymerisation $\bar{P}$, the average for the entire specimen, is defined as $\bar{P} = G/N$, where G is the mass of the polymer, and N the total number of polymer particles. Solution of this equation[7] gave the equation:

$$\frac{1}{\bar{p}} = \frac{4}{15}\frac{k_i\theta\rho}{z} \qquad (6)$$

where ρ is the radius of the working surface of the anvil.

Fig.8 gives the dependence of $1/M_m$ on θ for pressures of 1000 MPa and 2000 MPa and for temperatures of 293 K and 195 K. Data corresponding to degrees of transformation of 3% and above[53] were used, that is the descending branch of the dependence of the molecular mass on the angle of rotation of the anvil was treated. According to Eqn.(6), the slope of the straight lines is proportional to k_i; thus the rate of formation of the radicals in the specimen increases with increase in pressure and temperature.

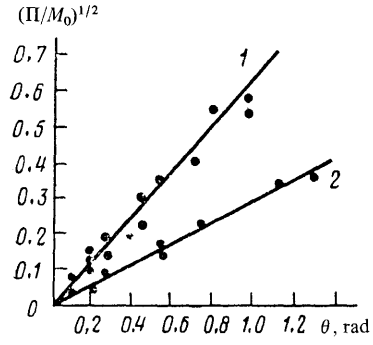


Figure 7. Dependence of (Π/M_0) on θ, obtained on anvils of different diameter[53] at 1000 MPa and 293 K: *1*) 20 mm, *2*) 10 mm.

Table 3. Rate constants and their ratio for the elementary stages of the polymerisation of acrylamide for SD + HP[7].

Conditions	$10^4\, k_p k_i/k_t$	$10^4\, k_i$	k_p/k_t
2000 MPa, 293 K	0.59	0.75	0.88
1000 MPa, 293 K	0.48	0.52	0.58
1000 MPa, 195 K	0.42	0.2	0.45

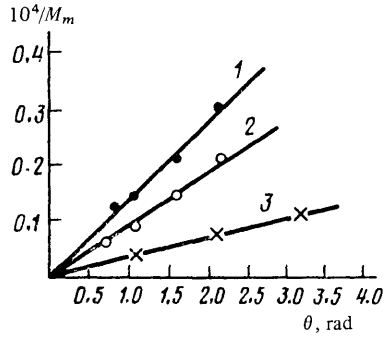


Figure 8. Dependence of the reciprocal of the molecular mass of polyacrylamide on the angle of rotation of the anvils under different conditions[53]: *1*) 2000 MPa, 293 K; *2*) 1000 MPa, 293 K; 3) 1000 MPa, 195 K.

The proposed mechanism of polymerisation and the mathematical m treatment of the experimental data carried out using the principle of stationary character make it possible to describe the dependence of P on θ and of π/M_0 on θ. This mechanism makes it possible to explain why the molecular mass of the polymer decreases at degrees of transformation greater than 3–5%; the decrease in molecular mass is due to the rapid increase in the concentration of active centres for polymerisation as the reaction proceeds[7].

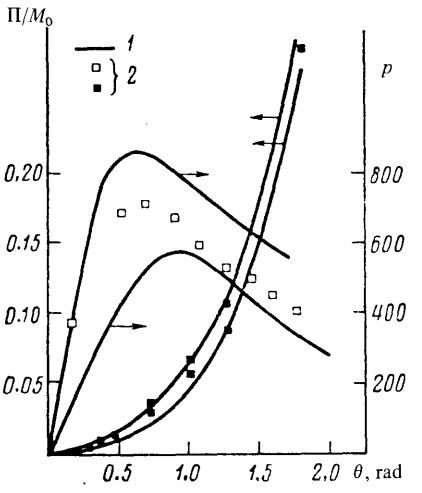


Figure 9. Dependence of the yield and degree of polymerisation of polyacrylamide on the angle of rotation of the anvils[7]: *1*) calculated curves, *2*) experimental data.

Eqns.(5) and (6) made it possible to calculate the rate constants of the elementary reactions and their ratios[7,53] (Table 3). Although Eqns.(5) and (6) describe the principal kinetic data satisfactorily, they do not explain, even qualitatively, the production of the maximum on the curves giving the dependence of the molecular masses on θ. It has been suggested[7,55] that the increase in the molecular mass of the polymer at low degrees of deformation is related to the non-stationary character of the process in the initial stage of the polymerisation. To verify this suggestion, the system of equations was solved without using the principle of stationary character[7,55]. The differential equations (3) and (4) were solved by numerical methods using the experimentally determined values of k_i and k_p^2/k_t (see Table 3) with variation of the quantity k_t/k_p. It was necessary, using the values of k_p^2/k_t and k_i, to select k_t/k_p to obtain curves giving the dependence of Π/M_0 on θ, of P on θ, and of P on Π/M_0 close to the experimental curves.

Fig.9 gives the experimental and calculated dependence of Π/M_0 on θ and of P on θ.[7] The theoretical curves calculated for $k_t/k_p = 10–20$ coincide to within 20–30% with the experimental curves for all degrees of conversion. Thus the results confirm that the polymerisation is non-stationary in the early stages of the deformation of acrylamide.

IV. CONCLUSION

The experimental data obtained indicate that under shear deformation conditions at a high pressure, solid organic compounds of different classes can polymerise at anomalously high rates, and can react by reaction paths which are not followed under ordinary conditions.

Measurements and calculations indicate that the rate constants of polymerisation with SD + HP may be 10^5 or more times the analogous constants characterising the liquid-phase reactions at the same temperatures and pressures. Under deformation conditions there may be a marked change in the selectivity of the chemical process. In a number of cases, side reactions which do not take place to a significant extent under ordinary conditions take place at rates comparable with that of the main reaction.

The reasons for the high reactivity of substances under SD + HP conditions have been insufficiently studied. Nevertheless, it should be noted that the dependence of the principal kinetic parameters (the degree of transformation, the concentration of radicals, the molecular mass of the polymer, etc.) on the shear deformation indicates that the duration of the elementary stages of the reaction of the interacting particles is very short, and the number of elementary acts is a function of the shear deformation. To explain this characteristic feature of processes under SD + HP conditions, two alternative mechanisms can be proposed. According to the first, under SD + HP conditions, strained and hence chemically activated bonds are produced in the reagent molecules and subsequently react with other molecules or their fragments in collisions, brought about by the motion of the substance on deformation. In the other possible mechanism, the bond, molecular fragment, molecule, or micro-region of the solid reagent, strained as a result of deformation, on subsequent deformation "ejects" the stored energy (relaxation); the potential energy of elastic deformation is converted into the vibrational energy of the molecules and individual bonds, which consequently show a high reactivity.

It is difficult at present to decide which of these mechanisms predominates under SD + HP conditions, since both explain the anomalously high rates of transformation and the weak temperature dependence of the reaction rate. In the first case, the mechanical stress applied to the bond can lower the activation energy of the reaction, and in the second case the high vibrational temperatures ensure high rates of transformation and are revealed in low values of the apparent activation energies. The elucidation of the mechanism responsible for the high reactivity of substances, and the determination of the reasons for the mixing of heterogeneous solid mixtures under SD + HP conditions at a level close to the molecular level, are important tasks in physicochemical studies under SD + HP conditions.

Another important problem is the determination of the types of chemical transformation which can take place during the deformation of solid reagents. At the present time, about twenty types of chemical reaction have been detected under SD + HP conditions. These include the addition to a $-C{=}C-$ bond of small molecules and functional groups (water, ammonia, the carboxyl group, the amide group, etc.), Diels–Alder reactions, the decomposition of peroxides, esterification, etc. These studies have shown that there are chemical processes favoured by SD + HP conditions, and on the other hand there are types of transformation which take place with difficulty or not at all on deformation of the compressed reagents. The reactions for SD + HP conditions are favourable include primarily the synthesis of macromolecular compounds. The largest number of studies carried out with SD + HP have been devoted to transformations of

this type. For these reasons, the results of the study of polymerisation processes with SD + HP are providing (and undoubtedly will continue to provide, in further extensions of these studies) a phenomenological and theoretical base for the development of the chemistry of solid organic compounds under conditions of deformation at high pressure in the compressed state.

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Zelinskii Institute of Organic Chemistry,

Academy of Sciences of the USSR, Moscow

Translated from *Uspekhi Khimii*, 53, 251-272 (1984) U.D.C. 541:127+64:547.39

Problems of Non-isothermal Character in Polymerisation Processes

S.P.Davtyan, P.V.Zhirkov, and S.A.Vol'fson

The results of the study of the radical polymerisation of vinyl monomers taking place under non-isothermal conditions, namely under purely adiabatic conditions, with transfer of heat to the surrounding medium, under the conditions of propagation of the polymer front, and the influence of hydrodynamics on the kinetics of polymerisation, have been reviewed. Various data on the ionic polymerisation of lactams, where the spontaneous heat production in the reaction is determined not only by the chemical source of heat release but also by the crystallisation of the resulting polymer, have been analysed. The results of the study of the condensation of epoxide compounds under the influence of amines under adiabatic conditions and under conditions of propagation of the polymer front have been discussed briefly.
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I. INTRODUCTION

Many processes in the synthesis of polymeric materials are characterised by highly exothermic reactions and low values of the coefficient of thermal conductivity of the monomer–polymer mixture. This combination of thermophysical characteristics of the polymerisation medium together with the reaction rates actually observed in practice often leads to superheating of the reaction mass and the appearance of a non-uniform space–time distribution of the temperature and the extent of the reaction. A consequence of the formation of these non-uniform fields is the difficulty of controlling the process and in a number of cases a deterioration in the properties of the polymeric materials formed.

Spontaneous heat production in a polymerising system may lead to a change in the thermal conditions such as a change from bulk polymerisation to a self-propagating polymerisation front, or may influence the concentration of macroradicals and the intensity of the manifestation of the gel effect, or may lead to "burn-out" of the initiator long before the consumption of the monomer, and to the start of polymerisation by thermal initiation. Effects of this kind lead to a significant change in the regular kinetic features and properties of the materials formed. The development of new energetically rational processes, and the intensification of existing processes, must involve the analysis of the kinetic characteristics of non-isothermal polymerisation.

The traditional approach to the study of the kinetics of polymerisation processes involves an analysis under isothermal conditions. At the same time, in practical technological problems, it is usually necessary to deal with non-isothermal conditions as such or with departure of the reaction from isothermal conditions as a result of the influence of various factors.

In the last ten years, at least two factors have led to an increased interest in polymerisation reactions under non-isothermal conditions. The first of these is the deeper knowledge of the inter-relationship between the conditions of synthesis and the structure and properties of polymers, which has led, in particular, to a sharp increase in the number of studies of the control of the molecular-mass distribution (MMD) and the influence of the MMD on the properties of polymers. The second factor is the trend towards the use of non-isothermal conditions to intensify industrial polymerisation processes in reactors of different type, and also to harden oligomeric systems and to obtain cross-linked structures directly in articles.

The present review examines and summarises for the most part work carried out in recent years by Enikolopov and co-workers.

II. FREE-RADICAL POLYMERISATION

Polymerisation by a radical mechanism, which is the simplest and has been studied in most detail, has become the principal object of study in the investigation of non-isothermal effects. This process can be carried out in practically all known thermal conditions, and the analysis of the consequent problems is important for practical applications.

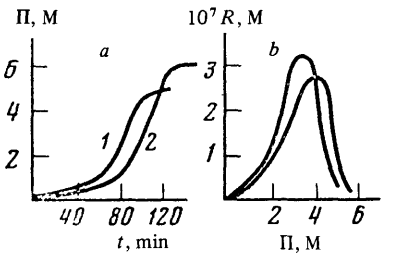


Figure 1. Change in the yield of polymer (П) (*a*) and the concentration of macro-radicals R (*b*) during adiabatic polymerisation[1]: *1*) quasi-stationary solution, *2*) exact solution; $I_0 = 10^{-3}$ M, $T_0 = 350$ K.

1. The Kinetics of Polymerisation Under Adiabatic Conditions

In the adiabatic polymerisation of vinyl monomers, depending on the difference between the activation energies for the decomposition of the initiator and for the termination of the chains, an adiabatic increase in the temperature of the polymerisation medium should mainly be reflected in the increased rate of decomposition of the initiator. Thus at sufficiently high rates of change of temperature, the use

of the principle of quasi-stationary concentrations (QSC) in the classical sense may become incorrect. In fact, numerical computer analysis of a kinetic scheme including initiation, propagation, and bimolecular termination shows[1] that there is a fairly marked difference between the quasi-stationary and the true solutions (Fig.1), the discrepancy between which depends chiefly on the magnitude of the heat of polymerisation (Q), the activation energies (E_i, E_t), and the pre-exponential factors (k_{i0}, k_{t0}) of the rate constants for initiation (k_i) and termination (k_t).

If in the equation for the concentration of macroradicals (R)

$$\frac{dR}{dt} = k_i(t)\,I(t) - k_t(t)\,R^2 \qquad (1)$$

the relative deviation of the true concentration of macroradicals from the quasi-stationary concentration ($\bar{R}$) is denoted by the quantity $\Delta = R/\bar{R} - 1$, then[2]:

$$\frac{d\Delta}{dt} = -\Delta(1+y)\,a(t) + \frac{1+\Delta}{2}\,\Psi(t) \qquad (2)$$

where

$$a(t) = \sqrt{k_i(t)\,k_t(t)\,I(t)};\quad \Psi(t) = \frac{1}{RT^2}(E_t - E_i)\frac{dT}{dt} + k_i(t);\quad y = R/\bar{R}$$

$I(t)$ is the concentration of the initiator, and T the temperature.

Analysis of Eqns.(1) and (2) shows that if $ta(t) \gg 1$ and $k_i(t)/a(t) \ll 1$, then $\Delta \to 0$, that is under non-isothermal conditions it is possible to use the QSC principle. In fact, the numerical solution of the system of kinetic equations for the adiabatic polymerisation of styrene, methyl methacrylate, and n-butyl methacrylate shows that for $ta(t) \geq 10^2$ and $k_i(t)/a(t) \leq 10^{-3}$ the QSC method can be used with sufficiently high accuracy.

Subsequently, the QSC principle was developed for cases in which it is possible to have the gel effect during adiabatic polymerisation; the conditions for the use of the QSC principle for the theoretical study of molecular masses and the MMD for the formation of the polymer were also studied[3].

The kinetics of radical polymerisation under adiabatic conditions when the QSC method is applicable have been studied theoretically[1,4,5]. The influence of various methods of initiation—photo- or radiation (W_i = const), thermal ($W_i = k_M M^2$), material ($W_i = k_i I$), complex ($W_i = k_{i1} I_1 + k_{i2} I_2$), and mixed ($W_i = k_i I + k_M M^2$) on the kinetics of formation and yield of the polymer were studied; here, W_i is the rate of initiation, and M the monomer concentration.

For the first three cases of initiation, the original kinetic equations can be solved in analytical form; the graphical representation of these solutions is given in Fig.2, which shows that for radiation (curve 2) or thermal (curve 3) initiation, the polymerisation gives 100% conversion, whereas for material initiation (curve 1) the conversion is much lower. The reason for the low yields for material initiation is that during the adiabatic increase in the temperature of the reaction mixture, complete "burn-out" of the initiator takes place long before the monomer is used up. The experimental study[6-11] of the kinetics of the radical polymerisation of styrene, methyl methacrylate, and n-butyl methacrylate under the influence of various peroxide initiators has shown that in accordance with theory, the yield of polymer formed does not exceed 40–50% of the original monomer concentration. Under specially selected conditions during the initiated adiabatic polymerisation of methyl methacrylate and n-butyl methacrylate, there is a gel effect[12], and in spite of the "burn-out" of the initiator, the yield of polymer may correspond to the practically complete consumption of the monomer. Since the realisation of this situation depends on the nature of the monomer, from the practical viewpoint, increasing the yield of polymer with material initiation is of considerable interest. For this purpose, a theoretical study was made[1] of the dependence of the yield of polymer on the initial conditions, the kinetic parameters, and the thermophysical characteristics of the monomer–polymer mixture. A significant increase in the yield can be achieved by using mixtures of initiators with different activation energies of decomposition.

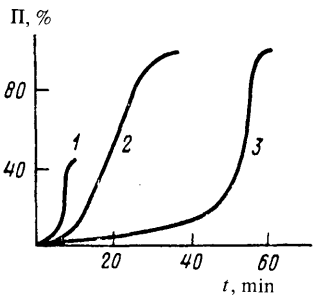


Figure 2. Kinetics of the adiabatic polymerisation of styrene for material (*1*), radiation (*2*), and thermal (*3*) initiation[1].

The influence of mixtures of different initiators on the kinetics of the polymerisation of styrene and methyl methacrylate using dicyclohexyl peroxydicarbonate (CPC), benzoyl peroxide (BP), t-butyl peroxide (tBP), cumyl peroxide (CP), and isobutyrodinitrile as initiators has been studied experimentally[13].

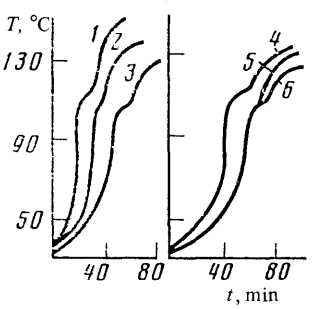


Figure 3. Kinetic curves for the polymerisation of methyl methacrylate under the influence of a mixture of initiators[13]: *1*) M_0 = 5.7, [CPC] = 0.22, [tBP] = 0.5; *2*) M_0 = 5.1, [CPC] = 0.2, [tBP] = 0.5; *3*) M_0 = 4.7, [CPC] = 0.22, [tBP] = 0.2; *4*) M_0 = 4.7, [CPC] = 0.1, [tBP] = 0.09; *5*) M_0 = 4.7, [CPC] = 0.05, [tBP] = 0.15; *6*) M_0 = 4.7, [CPC] = 0.05, [tBP] = 0.21 M.

The kinetics of the change in temperature during the reaction for initiation by a mixture of CPC and tBP are shown in Fig.3. The addition to the polymerisation system

of a second initiator (tBP) characterised by a higher activation energy leads to a change in the nature of the kinetic curves. A noteworthy feature is that the kinetic curves, in agreement with the theoretical results, show two inflections, indicating separate initiation in this system.

Comparison of the yields of polymethyl methacrylate and polystyrene obtained for initiation by a mixture of CPC with tBP or with CP with the yields for initiation by these initiators separately shows that in the first case the conversion increases by 60%, whereas the use of BP with other initiators is not effective, because of induced decomposition[14].

Under the conditions of adiabatic polymerisation, because of the continuous increase in temperature, the role of thermal initiation increases. For high degrees of transformation and high initial concentrations of monomer, thermal initiation may become the principal source of primary radicals. In fact, when the polymerisation of n-butyl methacrylate is carried out[11] without a solvent at higher temperatures (curve *1* in Fig.4*a*), the kinetic curves show a second abrupt change in temperature, due to thermal initiation. Dilution levels out the thermal polymerisation (curve *2* in Fig.4*a*), because of the low residual concentration of the monomer.

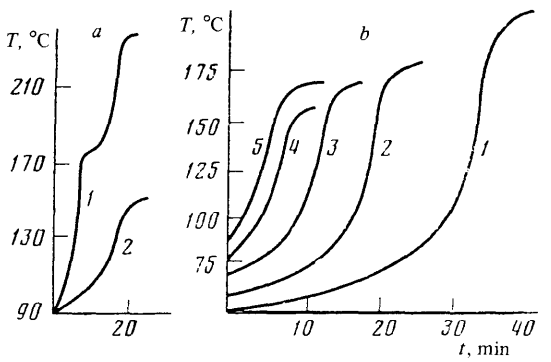


Figure 4. Kinetic curves for the adiabatic polymerisation of n-butyl methacrylate in the block (*a*, curve *1*; *b*, curves *1–5*) and in solution (*a*, curve *2*) for different initial temperatures[11,12].

The kinetics of the thermal polymerisation of styrene under adiabatic conditions was the subject of a special study[15] involving variation of the initial temperature and concentration of the monomer. To obtain a quantitative description of the kinetic curves, the authors cited carried out kinetic calculations assuming unimolecular, bimolecular, and termolecular mechanisms of initiation, and good agreement with experiment was obtained only for second-order kinetics.

In polymerisation under adiabatic conditions, complete decomposition of the monomer may be observed not only for thermal polymerisation but also when there is a gel effect. In fact, in a study of the polymerisation of n-butyl methacrylate in the bulk at an initial temperature of 50 °C,[12] an adiabatic increase in temperature was observed, corresponding to the practically complete consumption of the monomer (curve *1* in Fig.4*b*). With increase in the initial temperature of the reaction, there is a decrease in both the yield of polymer (at temperatures of 50, 70, 80, and 90 °C, the yields of polymer are 6.3, 4.5, 3.25, and 2.9 M respectively) and the final temperature of the system. The observed complete consumption of n-butyl methacrylate at 50 °C can in principle be attributed to an additional source of radicals, capable of bringing about thermal polymerisation. In this case, however, increase in the initial temperature of the reaction should lead to an increase in the rate of the thermal polymerisation itself, and hence to the complete consumption of the monomer, irrespective of the initial temperature of the reaction.

Thus this behaviour of the kinetic curves can be explained only by the gel effect in the reaction mixture. Comparison of experiment with calculations based on a kinetic model of the process makes it possible in this case to study the dependence of the rate constant of chain termination on the extent and temperature of the reaction.

The alternation of initiation and thermal polymerisation under adiabatic conditions is of methodological interest for the study of the mechanism of thermal initiation. In these cases, in the initial stage of the reaction, "burn-out" of peroxide impurities takes place, and all the subsequent information contained in the kinetic curves relates only to thermal polymerisation. Thus more reliable information on the mechanism of thermal initiation can be obtained by studying the polymerisation of vinyl monomers under adiabatic conditions, as was done for n-butyl methacrylate and styrene[12,15].

From the viewpoint of the determination of the elementary rate constants, a fact of considerable methodological interest is that at the moment of burn-out of the initiator, the quasi-stationary character with respect to the macroradicals breaks down, and post-polymerisation takes place; the latter can be studied using ordinary non-isothermal methods for determining elementary constants[16–21].

2. Nature of the Change in the Molecular Masses and the MMD in Adiabatic Polymerisation

The use of familiar methods (Laplace transformation, generating function method, etc.) for calculating the MMD function for radical polymerisation processes under adiabatic conditions involves considerable mathematical difficulties, because of the change in the rate constants with increase in the reaction temperature. Another limiting factor in the use of ordinary methods is that in adiabatic polymerisation, at the moment of "burn-out" of the initiator, the quasi-stationary character with respect to the macroradicals breaks down, so that to take detailed account of the characteristic kinetic features determined by the MMD of the final product, it is necessary to study the polymerisation without using the QSC method.

The nature of the change in the molecular masses and the MMD of the resulting polymer during the polymerisation under conditions when the QSC method is applicable or when this method is not applicable has been studied[1] in relation to the method of initiation.

For a constant rate of initiation up to high degrees of transformation, the mass-average ($\bar{P}_w$) and number-average ($\bar{P}_n$) molecular masses increase linearly with increase in the degree of transformation, but at the end of the reaction they decrease slightly, because of the consumption of the monomer. There is an analogous change in the ratio $\bar{P}_w/\bar{P}_n$, which is a measure of the polydisperse character of the resulting polymer. For thermal initiation, the ratios $\bar{P}_w/\bar{P}_n$ and $\bar{P}_z/\bar{P}_n$ ($\bar{P}_z$ is the *z*-average molecular mass) increase before the end of polymerisation.

For initiation by a material initiator, the values of $\bar{P}_w/\bar{P}_n$ and $\bar{P}_n$ decrease during the reaction as a result of an increase in the rate of decomposition of the initiator and a decrease in the lifetime of the macroradicals. In the initial stages of the reaction, $\bar{P}_n$ and $\bar{P}_w$ change in the same sense,

but subsequently, $\bar{P}_n$ decreases more rapidly than $\bar{P}_w$, since the formation of the low-molecular-weight polymer makes a more significant contribution to the first moment of the MMD function. For the same reason there is a slight broadening of the MMD of the resulting polymer.

For complex initiation (two initiators, initiator + thermal initiation), the curve giving the change in the instantaneous number-average molecular mass has several extremal points, due to the successive "burn-out" of the initiators or an increase in the role of thermal initiation with increase in the temperature of the system.

The moment of "burn-out" of the initiator has a fairly strong influence on the nature of the change in the MMD and the molecular masses, since the lifetime of the growing "live" chains may increase without limit. In this case, for a quantitative description of the adiabatic polymerisation, it is obviously necessary to analyse the MMD without using the QSC principle. For this purpose, the system of differential equations for the moments of the distribution of the "live" and "dead" polymers was solved numerically using a computer[1]. Analysis of the results shows that at low degrees of polymerisation, where the rate of bimolecular termination by a disproportionation mechanism is low because of the low concentration of macroradicals, the number-average molecular masses of the "live" and "dead" polymers increase and then decrease, and at the end of the polymerisation a new moderate increase in $\bar{P}_n$ for the "dead" polymer and a fairly intense increase for the "live" chains are again observed. For the "live" polymer, almost up to the end of the polymerisation, the ratio $\bar{P}_w/\bar{P}_n = 2$, after which, as the initiator is used up, it decreases to 1, due to the increase in the lifetime of the growing macromolecules, that is a change to "live" polymerisation.

The ratio $\bar{P}_w/\bar{P}_n$ for the "dead" polymer is close to 1.5 practically up to the end of the polymerisation, and it increases sharply only after the initiator has been used up. The increase in the polydisperse character of the "dead" polymer is also due to the "burn-out" of the initiator, so that the decrease in the rate of termination at the end of polymerisation leads to an increase in the length of the "live" chains by several orders of magnitude, and this has a stronger influence on the value of $\bar{P}_w$.

The results of the experimental study of the nature of the change in the MMD and the molecular masses in the adiabatic polymerisation of n-butyl methacrylate show complete agreement with these regular features[11].

As already noted, the determination of the MMD function using a Laplace transformation or a generating function involves considerable mathematical difficulties, and these methods can be used successfully only in those cases where the MMD function can be found analytically.

A method of finding the MMD function which eliminates these difficulties and is particularly effective in the analysis of non-isothermal polymerisation is therefore of interest[22,23]. The method involves essentially the reduction of the original system of differential equations for the "live" macromolecules to one equation in partial derivatives

$$\frac{\partial R(x,t)}{\partial t} + \frac{\varphi_2(t)}{N}\frac{\partial R(x,t)}{\partial x} = \varphi_1(t)R(x,t) \qquad (3)$$

where $x = j/N$; the number N is related to the chosen scale with respect to x, $\phi_1(t) = k_p(t)M$, $\phi_2(t) = \phi_1(t) + k_t(t) + k_t'(t)$, and k_t and k_t' are the rate constants for termination by recombination and disproportionation respectively. Eqn.(3) is solved by the method of characteristics.

The mass-average molecular mass and the ratio $\bar{P}_w/\bar{P}_n$ calculated by this method on a computer for the adiabatic polymerisation of styrene are given in Fig.5, where the points give the experimental data. The theoretical calculations show good agreement with experiment.

It should be noted that the maximum rate of polymerisation, corresponding to the maximum concentration of macroradicals, and the minimum value of $\bar{P}_n$, are reached for the same degree of polymerisation. The subsequent decrease in the concentration of macroradicals and increase in their lifetime leads to an increase in the molecular mass and a decrease in the rate of the process.

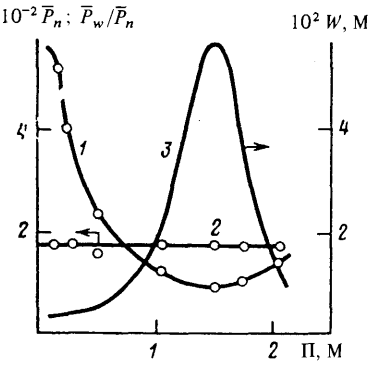


Figure 5. Change in the number-average molecular mass of polymerisation ($\bar{P}_n$, curve *1*), the width of the MMD ($\bar{P}_w/\bar{P}_n$, curve *2*), and the rate of polymerisation (W, curve *3*) during the adiabatic polymerisation of styrene[22]; $M_0 = 4.36$ M, $T_0 = 36$ °C; continuous curves—theory; points—experiment.

3. The Influence of Heat Removal on the Kinetics of the MMD

A periodic-action ideal-mixing reactor can be considered[24]. By changing the conditions of heat exchange at the walls of the reactor, it is possible to change the polymerisation conditions from isothermal to adiabatic. An indication of the non-isothermal character of the polymerisation process is provided by the Semenov parameter κ. For reactions with a high exothermicity and a high activation energy there is a sharp distinction, according to the Semenov parameter, between low-temperature (quasi-isothermal heating not more than 15–20 °C) and high-temperature (quasi-adiabatic, heating to 60–200 °C) polymerisation conditions. The intermediate zone is extremely narrow, and it is possible to speak of a critical value of the parameter κ. The intermediate zone becomes broader only for a low exothermicity and low activation energy of the process.

The change from one set of conditions to another is effectively illustrated by the dependence of the instantaneous number-average degree of polymerisation γ_n of the "live" polymer on the degree of transformation (α) (Fig.6).

For isothermal polymerisation, the quantity γ_n usually decreases monotonically with the degree of transformation (curve *1* in Fig.6). The appearance of heat production leads to a sharp decrease in the degree of polymerisation, since the activation energy of initiation is generally much greater than the effective activation energy of polymerisation. The change in γ_n may then be non-monotonic, and under low-temperature conditions, for example, the increase

in γ_n for the "live" polymer in the central phase of the process takes place as a result of cooling of the reacting mass (curve *2* in Fig.6).

The physical reason for the increase in the number-average chain length under high-temperature conditions is different. The rapid progressive increase in heating leads to the complete "burn-out" of the initiator, as a result of which the rate of initiation tends to zero, and $\bar{P}_n$ tends to infinity. Only macroradicals remain in the system, and very long polymer chains are formed (curve *3* in Fig.6).

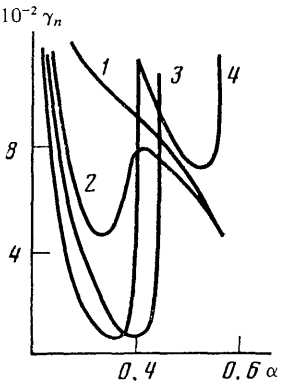


Figure 6. Dependence of the degree of polymerisation on the degree of transformation with heat removal under isothermal (*1*), low-temperature (*2*), and high-temperature (*3*) conditions and with thermal initiation (*4*).[24]

The qualitatively different changes in the degree of polymerisation during the reaction are responsible for the fundamentally different MMD under low-temperature and high-temperature conditions. Under the first conditions for degrees of conversion up to 0.5, the chain length is long and close to the initial quasi-stationary value, the distribution is narrow, and the heating increases the width of the MMD by not more than 5–20%. Under high-temperature conditions, the number-average molecular mass of the final polymer is much smaller (by factors of 3–10) than the quasi-stationary value, and the distribution is 2–3 times broader than the isothermal distribution (Fig.7). It should be emphasised that the narrow intermediate zone becomes broader only in the case of thermal "degeneration" of the process, that is for a small exothermicity of polymerisation or for a weak increase in the reaction rate with temperature.

Study of the detailed polymerisation kinetic scheme shows that allowance for chain transfer smooths out the differences in the polydisperse character between the quasi-isothermal and quasi-adiabatic conditions. With decrease in the degree of polymerisation under both sets of conditions, a marked decrease in the width of the distribution under high-temperature conditions is observed (curve *2* in Fig.7).

The existence of thermal initiation leads to separation of the process under high-temperature conditions into two quite distinct stages. At first, the initiator "burns-out" completely, and the heating of the system "includes" the thermal polymerisation mechanism. An interesting feature is that 100% conversion of the monomer is achieved only in the adiabatic case, and even with slight heat exchange, the consumption of the monomer leads to cooling of the reagents, and the reaction stops at $\alpha < 1$.

By itself, heat production in the reaction only broadens the MMD, but produces no qualitative changes in the nature of the distribution. A bimodal MMD may be produced, however, even in the simplest polymerisation kinetic scheme, if the heat exchange of the reactor is separated into two stages, and the temperature of the surrounding medium in the second stage is 30–40 K higher than that in the first.

In a continuous-acting ideal-mixing reactor, the constant supply of fresh reagents is responsible for a number of characteristic physical features of the processes[5], the most important of which is the possible existence of several stationary states of the reactor for the same values of the parameters. As in a periodic-action reactor, in this case also there are low-temperature and high-temperature conditions with corresponding types of MMD, determined by the kinetic scheme of the reaction.

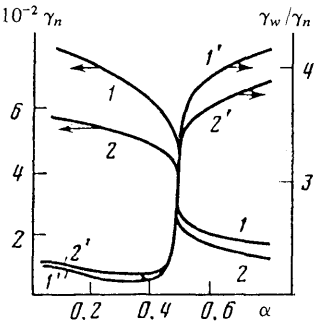


Figure 7. Influence of chain transfer on the degree of polymerisation (*1*, *2*) and the width of the MMD (*1'*, *2'*);[24] the curves were calculated without (*1*) and with (*2*) allowance for chain transfer.

4. Polymerisation During Propagation of the Thermal Wave

A classical example of the propagation of the front of an exothermic chemical reaction is provided by the burning of a flame in gaseous media. The comprehensive experimental and theoretical examination of this phenomenon is much in advance of the study of processes of this kind in condensed media. The analogy existing between the propagation of the front of exothermic reactions in gases and condensed media makes it possible to apply the results of classical theory to condensed systems.

The problem of the stationary velocity of the front of a chemical reaction was first examined in the theory of the combustion of gases by Zel'dovich and Frank-Kamenetskii[25–28]. The essential feature of this theory, namely the assumption that the coefficients of diffusion and temperature conductivity are equal, establishes a relationship between temperature and concentration, and makes it possible to reduce the system of two equations for diffusion and thermal conductivity to one equation, which unambiguously relates the rate of heat liberation to temperature. Because of the temperature dependence of the kinetic constants, the solution of the boundary problem requires additional assumptions, one of which is the assumption that the reaction zone is narrow and the chemical reaction takes place chiefly at temperatures close to those of the adiabatic

heating. In this case the boundary problem breaks down into two Cauchy problems: one in the range in which the reaction rate can be neglected, and the other in the range where the convective term in the thermal conductivity equation is neglected. The "joining" of the solutions for the two ranges makes it possible to obtain an analytical expression for the stationary velocity of the reaction front.

For the propagation of the front of a chemical reaction in a condensed medium, it is obviously impossible to assume that the coefficients of diffusion and thermal conductivity are equal, since they may differ by several orders of magnitude, and in most cases diffusion can be neglected.

The propagation of the front of an exothermic reaction in a condensed medium has been examined in a different formulation of the problem by a number of authors[29-37]. The conditions of existence and the unique character of the solution were studied, and various approximate methods for calculating the stationary velocity of the front were proposed. The method proposed in Ref.30 is based on the assumption that the reaction zone is narrow. It can be readily seen that for the general form of the dependence of the rate of heat liberation on the degree of transformation and temperature, the system of kinetic and thermal conductivity equations has a solution.

The approximation of a narrow reaction zone is based on the fact that, because of the high activation energy of the chemical reaction, most of the transformation takes place in a narrow range at temperatures close to the adiabatic heating of the reaction mixture. This makes it possible to replace the temperature by its maximum value in the equation for the temperature gradient in the reaction zone.

The approximation of a narrow reaction zone is not always applicable, however, even for high values of the activation energy of the chemical reaction. An important factor which restricts the applicability of this assumption in a number of cases is the nature of the dependence of the reaction rate on the degree of transformation. It has been shown[32,33], in particular, that for orders of reaction greater than unity, the assumption that the reaction zone is narrow is not correct. When there is retardation of the reaction, this approximation is unjustified even for high values of the activation energy.

An interesting characteristic feature of exothermic polymerisation reactions is the possible development of the process by a mechanism analogous to the propagation of a flame in a gas mixture. This was first pointed out in Ref.38. In subsequent studies[39-42] of the polymerisation of methyl methacrylate and triethylene glycol γ,ω-dimethacrylate under the influence of BP at a pressure of up to 5000 atm, propagation of the front of the polymerisation wave was established experimentally. Estimation of the velocity of the front showed that this phenomenon cannot be attributed to diffusion of active centres from the reaction zone into neighbouring layers with subsequent initiation of the reaction in these layers, since in this case the values of the velocity of the front should have been much lower than the experimental values. This gives grounds for assuming that the propagation of the polymerisation front in a cold mixture is thermal in character, that is it is similar to the normal propagation of a flame.

Special measurements[41] showed that there is no temperature gradient in the central part of the transverse cross-section of the reaction mixture. This means that under the conditions of the experiment, adiabatic propagation takes place, that is the front of the polymerisation wave is planar; the measured rate of displacement of the front is normal to this plane. The measured values of the rate of propagation of the thermal wave lie in the range 1–3 cm min^{-1}, depending on various parameters of the polymerisation mass. The structure of the front of the polymerisation wave, the influence of the concentration and nature of the initiator on the process of polymerisation propagation, and the role of pressure and the initial temperature have been studied[41,42]. It has been shown, in particular, that the stationary rate of propagation of the front of the polymerisation wave (u) increases with increase in the initial concentration of the initiator according to the law $u \sim I_0^{0.38}$.

Analysis of the thermodynamic characteristics shows that at atmospheric pressure, the boiling point of the monomer is reached for many monomers even at low degrees of transformation ($\leq$30%). Thus the propagation of the polymerisation reaction in this case must be accompanied by foaming of the polymerisation mixture[42]. Thus there exists a limiting pressure, below which stationary propagation of the polymerisation front is impossible.

When polymerisation is carried out under the conditions of propagation of the thermal wave with the reactor in a horizontal position and with mixtures having a low viscosity, convection is generally produced as a result of the existence of the heating zone. Convection cannot be eliminated even by using high pressures (up to 4000 atm). When the polymerisation reaction is carried out from above downwards in a column of liquid, convection is produced by the dropwise descent of the polymer formed. The experimental data show that in this case, for example with methyl methacrylate, breakdown of the front is not observed when a pressure above 1500 atm is used. Thus the prevention of convective breakdown of the front and boiling of the polymerisation mass is an important consequence of the use of high pressure in the propagation of the radical polymerisation reaction.

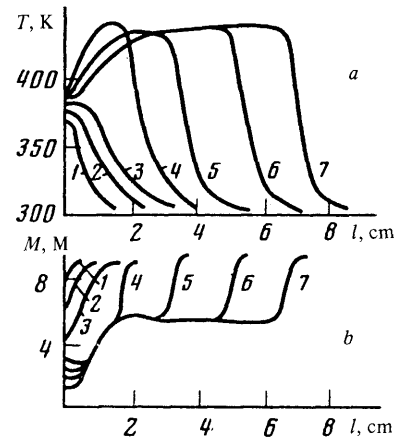


Figure 8. Profiles of the change in temperature (a) and the monomer concentration (b) along the direction of the reaction front after different times (s): *1*) 200, *2*) 800, *3*) 1600, *4*) 2400, *5*) 3000, *6*) 3600, *7*) 4200.[48]

The stationary propagation of the planar front of radical polymerisation with allowance for the specific characteristic features of the kinetics of the process has been studied theoretically by a number of authors[43-49]. The results of a numerical analysis[48], carried out without using the QSC method, show (Fig.8) that for material initiation in the presence or absence of the gel effect, the main mass of the

monomer reacts in a narrow temperature range at temperatures close to adiabatic heating. This result subsequently made it possible to use the approximation of a narrow reaction zone to find the stationary velocity of the front in analytical form.

The kinetic equations can obviously be simplified using the method of QSC with respect to the macroradicals. The study of this possibility for processes taking place under polymerisation wave propagation conditions[50,46] showed that with material initiation and assuming a narrow reaction zone, the conditions for quasi-stationary character have the form

$$\frac{k_t}{k_p} \gg 1; \quad \left(\frac{I_0 k_t}{k_i}\right)^{\frac{1}{2}} \gg 1$$

where the reaction rate constants are taken at the temperature of adiabatic heating.

The approximation of a narrow reaction zone made it possible to obtain analytical expressions for the stationary velocity of the polymerisation front with consumption of the initiator[46,47] and also for conditions under which its concencentration is constant[43]. In the first case, the analytical dependence of the limiting degree of transformation on the initial concentration of the initiator was obtained, and the width of the reaction zone estimated. The stationary rate of propagation of the polymerisation front is proportional to the initial concentration of the initiator to the power 0.4, which shows complete agreement with the experimental data. Comparison of the theoretical and experimental values of the stationary rate of propagation of the front and the limiting degree of transformation α_{lim} shows marked lack of agreement, however (Fig.9). Thus experiment showed practically complete consumption of the monomer, whereas the theoretically predicted degree of transformation is 0.6—0.7 (curve *1* in Fig.9*b*).

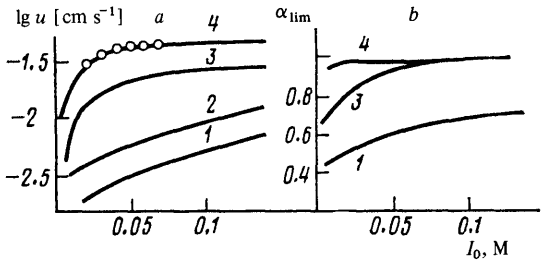


Figure 9. Dependence of the stationary velocity of the wave propagation front (u, cm s^{-1}) (*a*) and the limiting degree of conversion (*b*) on the initiator concentration; *1*) without allowance for pressure and the gel effect[44], *2*) with allowance for pressure, *3*) with allowance for the gel effect, *4*) with allowance for pressure and the gel effect[49]; points—experiment[41].

This lack of agreement between the experimental[39-42] and theoretical[43-46] results can be attributed to the existence of thermal polymerisation or the effect of high pressures and an extremely marked gel effect, not taken into account in the theory.

Allowance for polymerisation by thermal initiation should obviously lead to complete conversion. Published data[51] show, however, that the contribution of thermal polymerisation to the stationary velocity of the front is small (up to 3.5×10^{-3} cm s^{-1}). Thus a necessary step forward in the understanding of the nature of the discrepancy between theory and experiment was the study of the influence of pressure and the gel effect on the stationary velocity of the polymerisation front and the yield of polymer formed[49]. Fig.9*a* (curve *2*) shows that allowance for pressure leads to an increase in the magnitude of the stationary rate, but it still remains appreciably lower than the experimental value, and the limiting degree of transformation (curve *3* in Fig.9*b*) corresponds to complete consumption of the monomer only at values of I_0 equal to 0.1—0.15 M. The theoretical data show good agreement with experiment only when simultaneous account is taken of pressure and the gel effect (curves *4* in Fig.9*a* and 9*b*), and estimates for these conditions give a reaction zone width of 0.2 cm, which also shows good agreement with experiment.

As already noted, at high temperatures, thermal initiation may become the main source of radicals. At the same time, there have been practically no studies of its role in processes of radical polymerisation taking place under conditions of polymerisation wave front propagation, apart from a theoretical analysis of the influence of thermal initiation on the stationary rate of polymerisation, which shows that when there is no gel effect, for a reaction of first order with respect to the monomer, more acceptable values of the stationary rate are obtained in the approximation of a narrow reaction zone (curves *1* and *2* in Fig.10). When there is a gel effect, this approximation can also be used for higher orders of the reaction (curves *3* and *4* in Fig.10).

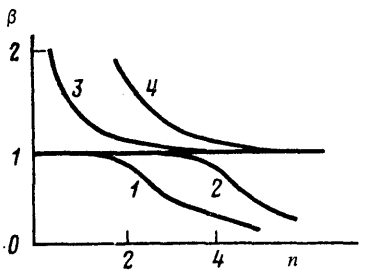


Figure 10. Ratio of the rates obtained from the results of analytical and numerical calculations of the rate of propagation of the front ($\beta = u_{anal}/u_{num}$) as a function of the kinetic order of the reaction (n);[51] the curves were calculated in the approximation of Ref.30 (*1*, *2*) and without it (*3*, *4*).

The kinetics of non-isothermal radical polymerisation in a periodic reactor without mixing have been studied theoretically and experimentally[52-54]. The results of numerical calculations and the analytical solution of the problem indicate that in these systems, for definite values of the parameters, values analogous to those for frontal polymerisation are observed. In fact, in the radical polymerisation of MTF-9 acrylate polyester, which has a high viscosity ensuring throughout the entire process heat transfer takes place by a purely conductive mechanism, the authors cited observed "layer" polymerisation conditions at atmospheric pressure[54].

There have been practically no experimental studies of the molecular masses and MMD in radical polymerisation under conditions of reaction front propagation. A theoretical analysis of the change in the molecular masses,

polydisperse character, and MMD of the resulting polymer has been carried out[47,51]. The calculations show that the average molecular masses decrease sharply behind the front of the thermal wave, but at the same time the decrease in the values of $\bar{P}_w$ and $\bar{P}_n$ is not the same, so that the polydisperse character of the resulting polymer at first increases because of the "burn-out" of the initiator (Fig.11*b*), but remains practically constant behind the wave front.

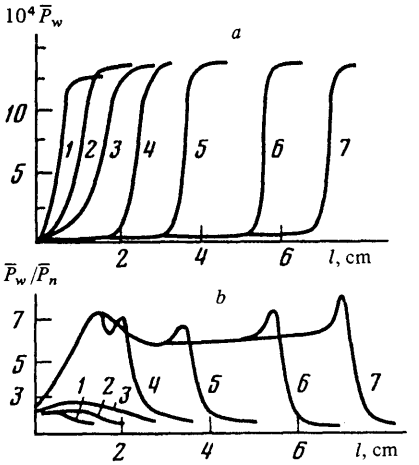


Figure 11. Change in $\bar{P}_w$ (*a*) and the width of the MMD (*b*) under front propagation conditions during the polymerisation of styrene[48]; $I_0 = 10^{-2}$ M, $T_0 = 300$ K, starting temperature 380 K; the numbering of the curves is the same as in Fig.8.

A broad MMD is a characteristic feature of polymerisation under reaction front propagation conditions. It should be remembered that for polymerisation under adiabatic conditions, the ratio $\bar{P}_w/\bar{P}_n$ for the final polymer is always appreciably greater than two, but for adiabatic polymerisation a narrow MMD may be preserved by stopping the polymerisation at the moment when the initiator "burns-out". This procedure is obviously impossible in principle for polymerisation under reaction front propagation conditions.

Chain transfer to the monomer or the solvent for frontal polymerisation leads to a decrease in the width of the MMD, and when this reaction is sufficiently intense, the MMD remains the most probable until the end of polymerisation.

5. Non-Isothermal Polymerisation in Tubular Reaction Vessels

The most important macrokinetic feature of polymerisation—the increase in the viscosity by several orders of magnitude—has a particularly marked influence on the course of the process in a tubular reactor. This influence is two-fold: firstly, there is appreciable distortion of the reagent flow rate profile, and secondly, there is a qualitative change in the integral characteristics of the process, primarily the pressure–flow rate characteristic, that is the dependence of the pressure drop (Δp) on the flow rate (q). The study of the process in the simplest one-dimensional version makes it possible to study the pressure drop–flow rate relationship, the longitudinal temperature profiles, and the influence of these parameters on the kinetics of polymerisation and the MMD of the products.

Polymerisation can take place under low-temperature or high-temperature conditions. In the absence of heat sources other than chemical sources, and when thermal conductance is negligible, increase in the consumption of the reagents leads to a proportionate displacement of all the points of the longitudinal profiles of temperature and concentration along the axis of the reactor. The temperature peak under high-temperature conditions ("hot spot"), with increase in the consumption, moves to the outlet from the reactor and may even leave the reactor[55]. There is then a unique relationship between the value of the flow rate of the reagents and the longitudinal temperature profile.

If the thermal conductivity in the axial direction is high (high thermal flux along the metal walls of the reactor), the relationship between the stationary states of the reactor and the flow rate become ambiguous. There exists a range of change in the flow rate within which one set of parameters corresponds to three different states of the reactor: low-temperature, high-temperature, and an intermediate unstable state. The arrival at specific reactor operating conditions depends on the initial conditions. In this case there is a complete analogy between the process of polymerisation in a tubular reactor and the process of combustion. With change in the consumption, flare-up or quenching of the process is observed, that is there is a change from low-temperature to high-temperature conditions and vice versa, and these changes show hysteresis. The range of non-unique solutions may consist of two separate regions of change in the flow rate, and there exists a range of values of the flow rate in which only high-temperature conditions are realised[56].

Heat liberation as a result of internal viscosity (dissipation of energy) may also lead to a non-linear change in the longitudinal temperature profiles. The mechanical source of heat increases in proportion to the square of the flow rate and to the viscosity of the liquid. Its contribution may naturally be particularly marked in polymerising systems. Studies have shown[57] that mechanical heat liberation plays the role of "trigger" for the change from low-temperature to high-temperature conditions, if the conditions of the process are close to the critical conditions for this change. Otherwise, the dissipation of mechanical energy has no qualitative influence on the operation of the reactor.

An important characteristic of a tubular reactor is the relationship $\Delta p(q)$, called the pressure–flow rate characteristic of the reactor. The form of this relationship is determined by the change in the distribution of the average (with respect to cross-section) viscosity along the length of the reactor with increase in the flow rate. The pressure–flow rate characteristic itself determines a number of regular features of the operation of the reactor, including qualitative features. For a polymerisation reactor, the $\Delta p(q)$ relationship is particularly complex. In the first place, the viscosity of the reacting mixture increases sharply during the reaction, and also changes with change in temperature. In the second place, as noted above, with change in the flow rate, non-linear changes take place in the longitudinal temperature profiles, and hence in the degree of transformation of the monomer. The viscosity undoubtedly depends on the molecular mass of the resulting polymer, but essentially no analysis of the effect of this factor has been published.

These characteristic features define the form of the $\Delta p(q)$ relationship. The marked increase in the viscosity is the reason for the basically non-monotonic character of this relationship. For very low values of the flow rate, the whole reactor is filled with very viscous polymerisation

products. Increase in the flow rate leads to the removal of products and to filling of a part of the reactor with less viscous reagents. The average viscosity in the reactor decreases rapidly, and the pressure drop $\Delta p \sim q \int_0^{\alpha} \mu(x)dx$ decreases. As a result, the $\Delta p(q)$ relationship at very low flow rates shows a clearly defined maximum[58], which is more marked, the greater the increase in the viscosity during the polymerisation. The flow rates corresponding to the maximum pressure drop also correspond to the almost complete transformation of the monomer at the outlet from the reactor ($\alpha \sim 0.95$).

A non-monotonic $\Delta p(q)$ relationship is also observed for the non-isothermal flow of an inert liquid, whose viscosity decreases rapidly with temperature. The decrease in the pressure drop with increase in the flow rate may take place as a result of the displacement of colder liquid, which has been able to cool during flow, by hotter and consequently less viscous liquid[59], or as a result of an increase in the dissipative heating[60]. Both of these effects, however, take place at extremely high values of the flow rate, much greater than those which can be realised in technological polymerisation processes.

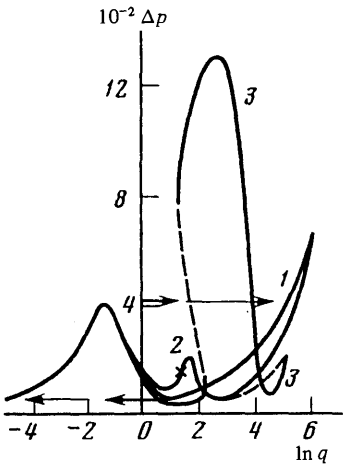


Figure 12. Pressure–flow rate characteristics of a tubular polymerisation reaction[60]: *1*) low-temperature conditions (the arrows indicate the hysteresis changes with change in the pressure drop); *2*) change from a dissipative source for the process to high-temperature conditions (the asterisk marks the point of change); *3*) high axial thermal conductivity (the broken lines are the branches of the curve for the unstable intermediate solution).

The above-mentioned change from low-temperature to high-temperature conditions for the process as a result of a mechanical source of heat may take place at comparatively low values of the flow rate. The form of the pressure–flow rate curve changes qualitatively, and new extremal points appear on it (curve *2* in Fig.12), since a complete rearrangement of the temperature and concentration profiles takes place. There is a sharp increase in both the heat production and the degree of transformation, so that there is competition between the temperature and concentration dependence of the viscosity, and either the former (in the case of solutions) or the latter (for bulk polymerisation) may predominate. The specific form of the $\Delta p(q)$ relationship may be extremely complex.

The situation is even more complicated when a decisive role is played by axial thermal conductivity. In addition to the maximum under low-temperature conditions (low values of the consumption), the pressure–flow rate characteristic shows a much larger peak under high-temperature "combustion" conditions, determined by the movement of the "front" along the reactor (curve *3* in Fig.12). In addition, branches of the $\Delta p(q)$ curve corresponding to stationary unstable states of the reactor exist.

In the experimental realisation of the process, it is possible to keep the flow rate or the pressure drop constant. In either case, several different stationary reactor operating conditions are possible, corresponding to the same value of the fixed parameter. With change in the parameter (for example the pressure drop in Fig.12), abrupt changes from one branch of the solution to another are possible. The points of the changes do not coincide, that is hysteresis is observed, and for Δp = const it is not thermal (as in combustion processes) but purely hydrodynamic.

The study of the flow rate profiles is possible only for a two-dimensional arrangement. The process has been studied for low-temperature conditions (or for the isothermal case).[61–63] As a result of the adhesion of the liquid to the walls of the reactor for an initial parabolic flow rate profile, the layers of liquid next to the wall are in the reactor for an extremely long time. The reaction in these layers takes place to a high degree of transformation, that is very viscous polymerisation products are formed, and the rate of flow at the wall decreases. Since the consumption is constant, there is a corresponding increase in the flow rate in the axial zone. The residence time of the reagents close to the axis decreases, so that there is a decrease in the degree of transformation of the monomer and the viscosity of the liquid, leading to an even greater increase in the rate of flow in the axial zone, etc.

This leads to the production of two quite distinct flow zones: a layer of very viscous slow-moving reaction products next to the wall, and a stream of reagents with low viscosity in the axial zone of the reactor, penetrating through the products (Fig.13). The ratio of these two zones depends on the flow rate, that is on the rate of supply of the reagents. To obtain uniform products at the outlet, it is necessary to have flow rates which are sufficiently low, so that the stream of unreacted liquid does not move out of the reactor. As a result of the "extension" of the flow rate profiles (Fig.13), the flow rate at the axis may be several tens of times greater than the average rate. As a result, there is a decrease in the flow rate (or an increase in the length of the reactor) necessary for complete polymerisation, compared with that calculated from the average residence time.

A study of the influence of the deformation of the flow rate profile on the MMD for "live" polymerisation[64] showed that the existence of two flow zones (essentially two fractions with markedly different molecular weights) may lead to the formation of a bimodal MMD at the outlet from the reactor.

An analysis of high-temperature polymerisation conditions in a tubular reactor with allowance for the distribution with respect to the cross-section of the velocity, temperature, and concentrations indicates that these conditions are unstable[65–67]. Within a definite range of change in the flow rates in the reactor, a polymerisation front is formed.

There exists a front stabilisation stage in which the rate of supply of the reagents is equal to the rate of "combustion". In the experiment, the duration of the stabilisation stage reached several tens of minutes. In this time interval, accumulation of viscous reaction products takes place ahead of the front, primarily with an increase in their viscosity, leading to an increase in the rate of flow in the axial zone. The rate of supply of the reagents becomes greater than the rate of "combustion", the front is deformed, and its central part is displaced towards the outlet from the reactor. The flow rate in the axial zone increases, with an increase in the rate of supply of the colder products to the less hot (as a result of curvature) front. The front cools and leaves the reactor.

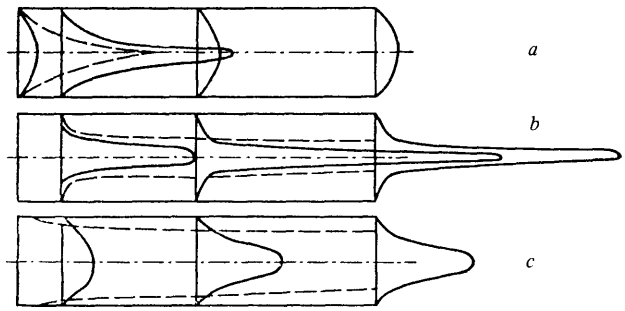


Figure 13. Profiles of the axial rates of flow in a tubular polymerisation reactor for different values of the flow rate: *a*) $q = 1$, *b*) $q = 10$, *c*) $q = 50$;[63] the broken line indicates the boundary of the layer of viscous products.

III. VARIOUS OTHER POLYMERISATION PROCESSES UNDER NON-ISOTHERMAL CONDITIONS

Many chemical reactions, although having smaller thermal effects and activation energies, are capable of taking place with spontaneous thermal acceleration under certain conditions. These reactions include various processes of ionic polymerisation, polycondensation, and vulcanisation (cross-linking).

Fairly reliable data on non-isothermal kinetics have been published for the anionic activated polymerisation of lactams and the polycondensation of epoxide compounds under the influence of amines, and these are examined in the present section. The non-isothermal kinetics of these processes make it possible to separate the common and distinctive features for various types of reaction taking place under non-isothermal conditions.

1. Anionic Activated Polymerisation of ε-Caprolactam

The anionic activated polymerisation of lactams (AAPL) opens up extensive possibilities for preparing constructional materials by "chemical" forming, that is directly from the monomers. The simplicity of the "monomer–article" technological scheme realised in the case of AAPL, however, hides major problems. These difficulties are related on the one hand to the complexity of the process itself and on the other hand to the spontaneous heat production in the reaction mixture. In spite of the fact that the exothermicity of the polymerisation of ε-caprolactam, for example, is only 3.2 kcal mole^{-1}, the adiabatic heating of the monomer–polymer mixtures may reach 70–90 K. In addition, the polymerisation of the lactam is accompanied by the simultaneous crystallisation of the resulting polyamide with a heat release of 6 kcal mole^{-1}, which also contributes to the increase in temperature. The spontaneous heating in AAPL is due not to high thermal effects of the chemical and physical processes taking place but to the high rate of the chemical reaction and the low values of the coefficients of thermal conductivity of the polymerising mixture.

The non-isothermal AAP of ε-caprolactam has been reported by a number of authors[68–73], who established that under adiabatic AAPL conditions for an initial polymerisation temperature of 150 °C and above, the polymerisation and crystallisation take place separately, whereas below 150 °C a combined process is observed. To exclude the influence of crystallisation on the kinetics of polymerisation, the process was studied either in the initial stages[74] or at temperatures above 150 °C.[75]

The development of experimental methods for separating information on the separate processes of polymerisation and crystallisation from the overall kinetics of the increase in temperature is obviously of interest.

A number of almost simultaneous papers[73,76,77] pointed out this new direction in the study of the kinetics of the AAP of lactams, chiefly ε-caprolactam. These papers described methods for the separate study of the kinetics of polymerisation and crystallisation taking place in parallel. Of these methods, the simplest and most reliable is the method[73] based only on experimental data. The results of this work can be examined briefly.

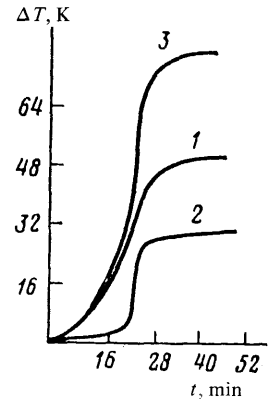


Figure 14. Kinetics of the change in temperature in the activated anionic polymerisation of ε-caprolactam;[73] *1*) polymerisation, *2*) crystallisation of the polymer, *3*) overall curve.

Independent experiments carried out at initial temperatures of 150 °C and 125 °C show that the actual temperature (T) of a reaction satisfies the respective equations:

$$T - T_0 = M_0 \frac{\Delta H_p}{c\rho} \alpha$$

$$\frac{T - T_0}{\alpha} = M_0 \frac{\Delta H_p}{c\rho} + \frac{\Delta H_{cr}}{c\rho} \eta$$

Here, M_0 is the initial concentration of the monomer, α and η are the extents of the polymerisation and crystallisation, ΔH_p and ΔH_{cr} the heats of polymerisation and crystallisation, c the heat capacity, and ρ the density.

Gravimetric determination of the yield of polymer during the polymerisation and use of the known value $M_0\Delta H_p/c\rho = 52$ made it possible to separate from the overall kinetic curve (curve *1* in Fig.14) the increase in temperature due only to polymerisation (curve *2* in Fig.14), and from the difference between curves *1* and *2* the change in temperature as a result of crystallisation (curve *3*). The limiting heating due to crystallisation obtained in this way agrees with the degree of crystallinity determined experimentally from the density[78].

A series of kinetic curves for polymerisation and crystallisation during the AAP of ε-caprolactam, obtained by this method, is given in Figs.15*a* and 15*b*.[79]

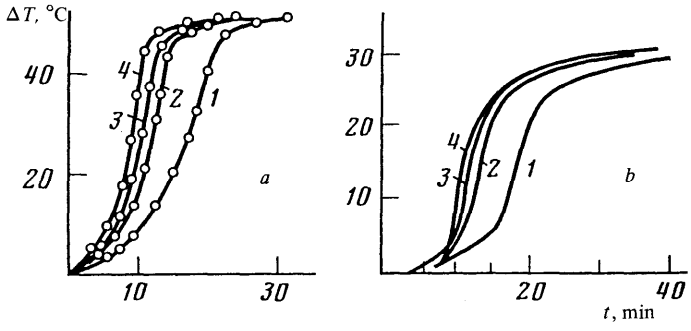


Figure 15. Kinetic curves for the polymerisation of ε-caprolactam (*a*) and the crystallisation of the polyamide (*b*) at different activator concentrations, M: *1*) 3.35×10^{-2}; *2*) 4.78×10^{-2}; *3*) 5.74×10^{-2}; *4*) 6.70×10^{-2}; $T = 125$ °C, concentration 3.35×10^{-2} M.[79]

The kinetic curves for the crystallisation of the resulting polyamide show three regions of increase in temperature: a slow increase, a range corresponding to a high rate of change in temperature, and the stage corresponding to the slow completion of the crystallisation process. The existence of three regions on the crystallisation kinetic curves, confirmed by the form of the dependence of η on α, is due to the sequence of stages involving nucleation, crystal growth, and secondary crystallisation, as confirmed by microscope studies of the morphology of the resulting polymers[80,81].

The methods developed for separating the kinetics of polymerisation and crystallisation make it possible not only to carry out a qualitative analysis of the kinetics of polymerisation and crystallisation but also to obtain a quantitative description of the kinetics of these complex processes[78,82-85].

Adiabatic thermometry is also of interest in the study of composition in combined polymerisation. The method is more valuable for copolymers having restricted solubility. A thermometric method has been proposed[86] for determining the composition of copolymers for the case of the anionic activated copolymerisation of ε-caprolactam with ω-dodecalactam.

Using published data[87] and assuming that in the adiabatic copolymerisation of ε-caprolactam with ω-dodecalactam the product $c\rho$ remains constant (the increase in the heat capacity is compensated by the decrease in the density), the authors cited obtained the equation

$$\Delta T_{cop} = \Delta T_{cl} N_1 + \Delta T_{dl} N_2 \qquad (4)$$

where ΔT_{cop} is the total increase in temperature due to adiabatic copolymerisation, ΔT_{cl} and ΔT_{dl} the adiabatic heating due to the polymerisation of caprolactam and dodecalactam, and N_1 and N_2 the mole fractions of the monomers in the copolymer.

By taking account of the fact that the values of the adiabatic heating for ε-caprolactam and ω-dodecalactam are 52 K and 20 K respectively and measuring the degree of transformation, it is possible, from the kinetic curves for the increase in temperature and a modification of Eqn.(4), to determine the composition of the copolymers formed for different initial ratios of the monomers.

Fig.16 gives the change in the composition of the copolymer during the reaction, together with data on the composition, obtained by ^{1}H NMR and elemental analysis. The good agreement of the values obtained indicates that the approach developed for the determination of the composition of the copolymers from adiabatic thermometric data is correct.

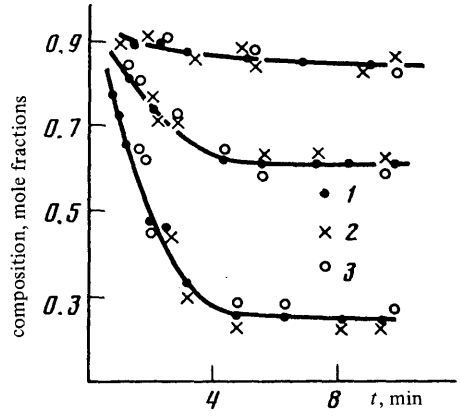


Figure 16. Kinetics of the change in the composition of the copolymer during the adiabatic copolymerisation of ε-caprolactam and ω-dodecalactam from data obtained by thermometry (*1*), ^{1}H NMR (*2*), and elemental analysis (*3*).[86]

There are no published experimental data on AAPL under the conditions of the propagation of a polymerisation wave. Studies of this kind may be of practical interest, in relation to the development of new methods for obtaining thick-walled monolithic articles based on polyamides.

A number of theoretical studies[88,89] showed the existence of a single thermal wave for combined processes of polymerisation and crystallisation. These results make it possible to formulate the conditions for carrying out frontal polymerisation experimentally for AAPL processes.

2. The Polycondensation of Epoxide Oligomers With Amines

The kinetics of the hardening of epoxide oligomers with different molecular masses under the influence of *m*-phenylenediamine (*m*PDA) under adiabatic conditions have been studied[90,91]. For the same initial reaction conditions,

increase in the molecular mass of the original oligomer leads to an increase in the rate of hardening. The authors cited attribute this to the catalytic effect of the hydroxyl groups, whose concentration increases with increase in the molecular mass of the oligomer. A quantitative description of the kinetic data was proposed.

Subsequently, on the basis of this approach, it was shown possible to harden epoxide oligomers under conditions of reaction front propagation[92].

Characteristic profiles of the change in temperature with time in the reactions of the epoxide oligomer ED-20 with *m*PDA and of ED-20 with polyethylenepolyamine are given in Figs. 17*a* and 17*b* respectively. After the thermal wave reaches stationary conditions, both the current reaction rate and the limiting temperature are the same in different layers. This means that the same quantity of epoxide groups reacts in each layer.

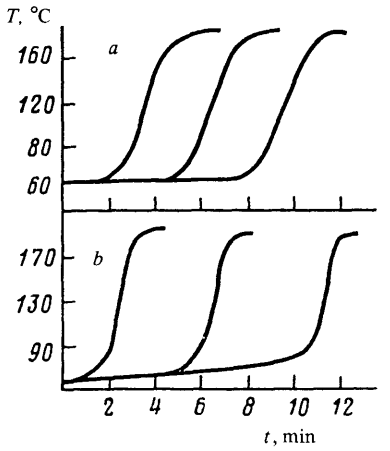


Figure 17. Temperature–time profiles for the hardening of epoxide resins in the presence of amines under thermal wave conditions[92]; temperature 60 °C (*a*) and 30 °C (*b*).

Special measurements showed that the temperatures at the surface of the thermal wave are the same, that is adiabatic propagation of the reaction front takes place in the experiment. Studies of the influence of the initial concentrations of the amine (A_0) and the epoxide groups (E_0) on the stationary rate of propagation of the wave show that $u \sim A_0^{0.63} E_0^{0.73}$. Increase in the initial temperature of the reaction mixture leads to an increase in both the maximum rate and the stationary rate, but since the maximum reaction rate increases more rapidly than the stationary rate, degeneration of the hardening front was observed at temperatures greater than 40 °C for PEPA and 80 °C for *m*PDA. This degeneration of the thermal wave, that is the change from frontal hardening conditions into volume hardening conditions is generally due to low values of the activation energy of the reactions taking place (8–10 kcal mole^{-1}).

The dynamics of the hardening of epoxide compounds by amines under conditions of thermal wave propagation have been studied by numerical methods[93].

Analysis of the solutions obtained shows that there are two reaction front propagation zones. The first corresponds to non-established conditions, and the second to established conditions, that is to stationary propagation of the hardening front.

An important conclusion from the comparison of the temperature and conversion profiles is that under stationary conditions the temperature profile is considerably in advance of the conversion profile. This means that the main mass of the product under conditions of stationary propagation of the thermal wave is formed in a narrow temperature range close to the adiabatic heating of the reaction mass. The influence of the initial concentrations of epoxide groups (E_0) and amine (A_0) and the kinetic and thermophysical parameters on the rate of propagation of the wave has also been analysed. The observed relationship, $u \sim A_0^{0.65} E_0^{0.8}$ is confirmed experimentally[92].

The approximation of a narrow reaction zone has been used[94] to find an analytical expression for the stationary velocity of the hardening front, and this again shows good agreement with experimental data.

* *
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The material examined in the present review on polymerisation processes of different type taking place under non-isothermal conditions shows that the interpretation is complicated by the need to take account of the thermophysical characteristics of the system, the temperature dependence of the parameters, and a number of other factors.

The development of the theory of processes of this kind is making it possible, however, to use these complications to achieve a marked increase in the amount of kinetic information extracted from the kinetics of the process being studied.

A most important aspect of the study of non-isothermal kinetics is the rational allowance for the dynamics and distribution of the heat of reaction; this is necessary when planning polymerisation processes in large systems, for example in the chemical forming of large models. The approaches described in the present review provide a basis for developing new energetically rational processes, and also for intensifying existing technological processes.

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Branch of the Institute of Chemical Physics,
Academy of Sciences of the USSR,
Chernogolovka,
Moscow Region

Translated from *Uspekhi Khimii*, 53, 273-289 (1984) U.D.C. 678.072 + 678.073

The Formation, Structure, and Properties of Epoxide Matrices for High-strength Composites

B.A.Rozenberg and E.F.Oleinik

The results of studies of the kinetics and thermodynamics of the formation, and the structure and properties, of epoxide cross-linked polymers, carried out in the last 7-8 years in the Institute of Chemical Physics of the Academy of Sciences of the USSR, have been reviewed. The molecular, topological, and supermolecular structures of epoxide polymers have been examined, and the relationship between the properties shown by these polymers in the vitreous and rubber-like states and their structure has been analysed. The progress made in the directed modification of the physicomechanical properties of epoxide binding agents have been discussed. The characteristic features of the structure and properties of epoxide polymers formed at the boundary with a solid surface have been examined.
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I. INTRODUCTION

A central problem in the design and production of articles of composite materials is the need to choose a polymer matrix ensuring the maximum realisation of the possibilities provided by the high-strength reinforcing fibres. This problem has many facets; one of its most important aspects is the relationship between the structure of a polymer matrix and its properties on the one hand, and the relationship between the conditions of synthesis and the structure on the other.

The present review examines the principal results of work carried out under the general direction of N.S.Enikolopov and directed towards the solution of the above problems. Densely cross-linked epoxide polymers, whose applied and technological properties at present make them the most promising binding agents for high strength composites, were examined in these studies. Individual aspects of these studies have already been summarised in a monograph[1] and a number of reviews[2-15].

The structure of polymers is usually classified as molecular and supermolecular. In the analysis of the structure of cross-linked polymers, in contrast to linear polymers, it is necessary to introduce another level of structural organisation of polymers, which has been called the topological; it characterises the degree of connectedness of the elements of the polymeric system. The terms linear, branched, ladder, or cross-linked polymer characterise the topological level of its organisation, a quantitative measure of which is provided by the distribution function of the corresponding element of the structure of the polymer system: branching between the chains, rings, etc.

The different levels of structural organisation of a polymer determine its various properties. There is in principle no unique simple relationship between all the levels of structural organisation, but a change in structure at any of the levels considered may have a significant influence on the properties of a polymer.

For an understanding of the various physicomechanical properties of a polymer it is first necessary to have a detailed and adequate description of each of its levels of structural organisation, and the practical problems of present-day materials science require a quantitative description. Progress in theory makes possible in most cases a quantitative description of the molecular and topological levels of structural organisation, but unfortunately this usually cannot be done at the supermolecular level.

The possibility of a quantitative description of the molecular and topological structure of a polymer, however, does not eliminate serious difficulties, related primarily to the fact that the relationship between the micro-characteristics, which adequately describe the molecular structure and topology of the polymer, and the macroscopic properties of the material in many cases is unknown. This is characteristic chiefly of polymer matrices in the vitreous state, which is the main working state of the polymer in a composite. Thus the search for the regular features establishing this relationship is one of the most important directions in present-day studies in the field of polymers and composites based on them.

II. STRUCTURAL ORGANISATION OF EPOXIDE NETWORKS

1. Molecular Structure

It is first of all necessary to find the characteristics of the molecular structure of the original epoxide oligomers, which are usually synthesised by condensing epichlorohydrin and compounds containing a mobile hydrogen atom—phenols, alcohols, acids, amines, amides, etc.

The most widely encountered are epoxide oligomers based on diphenylolpropane, the output of which makes up more than 90% of the total production of epoxide resins. It is for this compound and corresponding model compounds that the most important regular kinetic features of the formation of epoxide oligomers have been studied, and the mechanism of the process established.

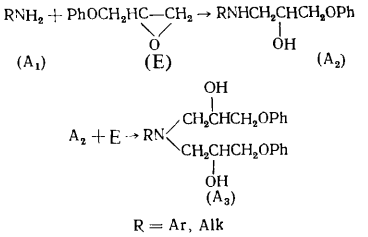
Epoxide oligomers are usually obtained by the reaction of epichlorohydrin with phenol; the epoxide ring of epichlorohydrin reacts with the phenolic hydroxyl group[16-18]. The reaction takes place by an ionic mechanism and is catalysed by bases. As a result of this reaction there is an increase in the molecular mass of the oligomer, and an excess of epichlorohydrin in the reaction system ensures the production of final oligomers which are bifunctional with respect to the epoxide groups. The main reaction, however, is always

accompanied by side reactions, involving mainly the consumption of epoxide groups in solvolysis and addition to internal secondary hydroxyl groups of the oligomers[19], leading to a change in the functionality and molecular structure of the final oligomer. The products sought are formed mainly in the first stage of the synthesis[20,21], whereas in the later stages an increasing contribution is made by side reactions[22,23].

Studies carried out have established the molecular structure of epoxide oligomers, produced kinetic models of the processes involved in their synthesis, which describe the process quantitatively[24–27], and developed new methods for carrying out the synthesis, which make it possible to increase the proportion of the main reactions in the production of the structure and functionality of the oligomers and to decrease the rate of side reactions[28–31]. The establishment of the relationship between the molecular structure and the molecular-mass distribution (MMD) of the resulting oligomers and the conditions of the process has made it possible to control the process to obtain epoxide oligomers with a given molecular structure and given properties[32]. The method of carrying out the process developed by N.S.Enikolopov and co-workers has formed the basis of an industrial method for the synthesis of diane epoxide oligomers by a continuous technological scheme.

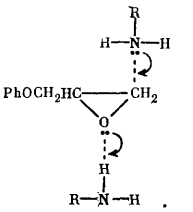
An extensive cycle of studies has also been carried out to establish the molecular structure of cross-linked epoxide polymers, obtained by hardening thoroughly purified and characterised epoxide oligomers and individual bifunctional monomers. In the course of these studies it has been possible not only to solve the principal problem being tackled, namely the production of binding agents with the required set of properties[1–12,33–36], but also to determine the principal regular kinetic features of the processes involved in the hardening of epoxide oligomers by various hardening agents[37–62], to establish a number of previously unknown details of the mechanism of these processes[7–12,36,39,41,44–52], to obtain a quantitative description of these processes and to determine the values of the thermodynamic and kinetic parameters[8,12,14,63–68], to establish the relationship between the reactivity and the chemical character of the reagents[50,69–71], to develop the principles of the rational choice of a hardening system and to control the molecular structure of the resulting three-dimensional network, and to establish scientifically based principles for selecting the hardening conditions to ensure intensification of the process and the production of materials with required properties[8,14,63].

In this cycle of studies, particular attention has been paid to the investigation of the kinetics and mechanism of the processes involving in the hardening of epoxide oligomers under the influence of amines, which are widely used in practice as hardening agents. The main reactions† taking place in this process can be represented by the following scheme:



† For simplicity, the reactions for the monofunctional compounds are given.

Before these studies, the mechanism of the opening of the epoxide ring under the influence of nucleophilic reagents was disrupted; it was not clear whether this reaction took place directly, or whether electrophilic cooperation was necessary. The studies[7,8,10,12,39] showed that the opening of the epoxide ring under the influence of nucleophilic reagents requires electrophilic cooperation, that is preliminary activation of the epoxide as a result of its reaction with some nucleophilic reagents. The idea of the need for activation is the key to the understanding of the regular kinetic features of the reaction of epoxide compounds with various nucleophilic compounds, including amines. This viewpoint makes it possible to understand the observed possibility of the non-catalytic reaction of epoxide compounds with primary or secondary amines and the second order of the reaction with respect to the amine[10,23,36]. In this case, one amine molecule acts as the nucleophile reagent, and the other as the proton donor. The transition state can be represented as follows:



A second important conclusion about the mechanism of the reactions studied is that the components of the reacting system, that is the starting materials and reaction products, are combined in hetero- and homo-complexes, characterised by different reactivities. The formation of these complexes may be both intermolecular and intramolecular; their existence has been reliably proved, and the thermodynamic parameters of complex formation determined[7,8,10,12,41,52,53,64,68].

It is only on the basis of ideas about complex formation in these systems that it is possible to understand such characteristic features of the kinetics of the reactions of epoxy-compounds with primary and secondary amines as the extremely unusual simultaneous reactions of self-acceleration and self-inhibition, the catalytic and inhibiting action of various solvents, the clearly defined *ortho*-effect of a number of substituents in aromatic amines, etc.[7–12,37,44,45,52,54].

The mechanism of the processes involved in the hardening of epoxide oligomers under the influence of amines is extremely complex; to a first approximation it can be described by a kinetic scheme which takes account of all the electron-acceptor interactions of the original reagents and the reaction products with one another. The kinetics of the processes of the hardening of epoxide oligomers under the influence of aromatic amines (at moderately high temperatures $t < 150$ °C) and the molecular structure of the resulting polymer are described almost completely by this scheme. At higher temperatures, condensation of the hydroxyl groups formed with unreacted epoxide groups and with one another also takes place, leading to the formation of additional cross-linking sites[59].

When primary or secondary aliphatic amines or aromatic amines with a nitrogen-containing heterocyclic ring are used as hardening agents, the polycondensation reactions are accompanied by anionic polymerisation of the epoxide oligomers under the influence of tertiary amines[10,12,36,46–49]. This gives a polymer which has the chemical structure of a simple polyether and which contains as terminal groups

double bonds of the vinylidene type, hydroxyl and alkyl groups, or a tertiary amino-group. These terminal groups are obtained by the decomposition of the active growing centre—the quaternary ammonium alkoxide—in several directions and subsequent secondary initiation[12,46-48].

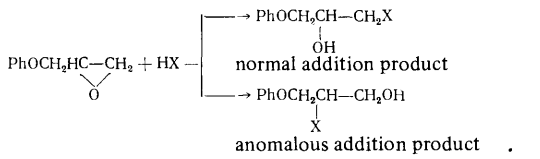
If the tertiary amine used is a nitrogen-containing heterocyclic compound such as pyridine and its derivatives, a new reaction takes place, leading to opening of the pyridine ring[46-48]. In this case the resulting polyene structure becomes a fragment of the polyether chain. The molecular structure of the polymer obtained is very complex; nevertheless, it can be reliably predicted if the detailed reaction mechanism is studied and the kinetic characteristics of the elementary stages of the process determined.

Analogous investigations directed towards the study of the kinetics and mechanism of the reactions and in the final analysis the establishment of the molecular structure of the resulting epoxide polymers are now being carried out with other hardening agents—phenols, alcohols, carboxylic acids, acid anhydrides, etc.[16-29,33,56,57]

The first results obtained in these studies confirmed the basic ideas about the important role of complex formation and the need for electrophilic cooperation in the reactions of nucleophilic addition of reagents to an epoxide ring. In contrast to amines, however, in a number of cases the reaction can also take place by an ionic mechanism.

A characteristic kinetic feature of the condensation of phenols and carboxylic acids with epoxides is that the product of the addition of a second molecule of the epoxide compound to the hydroxyether can be formed not only in succession, but also in parallel, by the direct reaction of two molecules of the epoxide–phenol (or carboxylic acid) complex[56,57].

Finally, new data on the determination of the direction of the opening of the epoxide ring are of considerable interest. A detailed study carried out by different NMR methods[33,36] showed that, contrary to the widespread view that normal addition takes place preferentially in nucleophilic attack at the epoxide ring, an appreciable proportion (up to 50%) corresponds to the anomalous addition of the nucleophilic residue X:



A number of studies have been devoted to the determination of the stability of epoxide polymers to the action of high temperatures and atmospheric oxygen. A detailed study of the thermal[72] and thermo-oxidative[73] degradation of cross-linked polymers based on the diglycidyl esters of diphenols with aromatic and aliphatic amines has been carried out by field mass spectrometry. Analysis of the products of the thermal and thermo-oxidative degradation of low-molecular-weight compounds[74] modelling the structure of the polymers studied showed that the weakest are the bonds $C^{\beta}-C^{\alpha}N$ in the hydroxypropylene bridge HC–CN in the aliphatic amine and $C-C_6H_4$ in the diphenylolpropane part of the chain, and the entire degradation process is described by a radical-chain mechanism. The process is initiated by the oxidation of the aliphatic parts of the polymer by atmospheric oxygen and the subsequent decomposition of the hydroperoxides formed. Chain transfer to heteroaliphatic parts of the polymer gives aminyl, alkyl, and aroxyl macro-radicals, whose decomposition gives derivatives of phenols, acetaldehyde, acetone, formaldehyde, and $H_2C{=}NCH_3$.[75]

With longer exposure to oxygen there is a decrease in the temperature of the appearance of those degradation products which are identical to the products of the thermal decomposition of the polymers in a vacuum. The thermo-oxidative degradation gives a large quantity of heavy products with masses 1.5–2.5 times the mass of the original model compound. The oxidation of secondary NH groups, which have not reacted with the epoxide, in the derivatives of aromatic amines gives stable aminyl and nitroxyl radicals, which inhibit the degradation, and in the derivatives of aliphatic amines gives the aminyl radical $\sim CH_2CH_2\dot{N}CH_2CH_2(OH)\sim$, which is actively involved in chain transfer. The dehydration process is the highest-temperature process both under conditions of the action of oxygen and in the subsequent degradation of the polymer in a vacuum.

2. Topological Structure

Analytical methods for describing the topological structure of cross-linked polymers suffer from the significant disadvantage that they do not make it possible to take account of the existence in the networks of rings of different size and complexity[1]. It is this feature, however, that determines the topological structure of the polymer network. Ring formation has a significant influence on the proportion of elastically active chains, which determine the mechanical behaviour of the polymer networks above the vitrification temperature. Allowance for this feature in different versions of the kinetic theory of high elasticity is usually made by introducing an empirical parameter—the front factor[1]. These difficulties have been successfully overcome by the development of a statistical topological model of the structure of cross-linked polymers, which has made it possible to establish a quantitative relationship between the chemical structure of the starting materials, the mechanism and conditions of the process of network formation, and the topological structure and various mechanical properties of networks in the highly elastic state[1,6-8,60,61,76-80].

The model of the structure of a densely cross-linked polymer was based on the view of a network as a set of randomly connected rings with a certain size distribution. The ring, that is a minimal closed contour in the network structure, was taken as the elementary structural unit. This approach made it possible to make specific the problem of describing the topology of the network structure and to reduce it to the determination of the distribution of the rings with respect to size. The process of formation of the network structure by the condensation of bifunctional molecules of diepoxide and tetrafunctional molecules of diamine was modelled on a computer by the Monte Carlo method. The scheme for the model process took account of intramolecular cross-linking (ring formation) both in the pre-gel region and in the later stages of the reaction, beyond the point of gel formation. The algorithm of the calculation made it possible to examine the influence on the kinetics of formation and topology of the network of such factors as monocyclisation, different ratios of the original reagents, differences in the reactivities of the functional groups of the reagents, and the change in reactivity during the reaction. Experimental analysis of the gel and sol fractions of the hardened systems confirmed the adequacy of the model of a real network system[78].

Berling and Oshmyan[81] were the first to describe the regular kinetic features of network formation; in particular, they predicted and detected a decrease in the reaction rate constant in the kinetic range in the later stages of the hardening reaction as a result of the high topological complexity of the system. The increase in the topological complexity of the system during the process leads finally to a non-trivial

physical effect. In stoichiometric mixtures, the reaction in principle does not go to completion, in spite of the presence in the system of a sufficient number of functional groups, capable of reacting. This limit of the reaction (yield < 100%), called the topological limit[77], appears because the reactive groups, which during the process have entered different topological formations in the network, cannot meet and react with one another even in the complete absence of diffusion restrictions.

The statistical model developed made it possible to carry out a quantitative analysis of the equilibrium elasticity of a network polymer in the rubber-like state. Because of the small dimensions of the chains between the nodes in the systems studied, this analysis could not be carried out within the framework of the traditional concepts of the kinetic theory of high elasticity. In the rubber-like state, the equilibrium elasticity of the network is determined by the elasticity of the chain between the nodes and by the topology of the network polymer. It has been shown[79] that by applying a mechanical stress to the boundaries of a model polycyclic network it is possible, by a numerical method on a computer without the use of any empirical parameters, to find the distribution function of the stresses in the chains between the nodes and the equilibrium modulus of elasticity of the network with allowance for the details of its molecular structure. Experimental verification of the theory showed excellent quantitative agreement between the results of the calculation and the experimental data, that is the proposed model provides an adequate description of the structure and equilibrium elastic properties of the networks. The observed agreement in the values of the modulus of elasticity indicates that all the non-uniformity of a real network lies within the limits of the statistical scatter. Spatial non-uniformity in the distribution of the reagents, for example as a result of micro-synergesis, would obvious lead to a decrease in the value of the equilibrium modulus of high elasticity E_∞. This conclusion is confirmed by an analysis of the topological structure and the equilibrium elasticity of the network systems, which show a conformational tendency to undergo monocyclisation reactions[60,61].

The topological model of a network polymer has been used successfully in a theoretical analysis of the durability and the nature of the breakdown of the network in the highly elastic state[79]; the undoubted advantage of this model for solving this problem lies in the possibility of taking account of the non-uniform character of the unloading of the chains between the nodes as a result of the topological non-uniformity of the network. Numerical modelling also made it possible to obtain information on the conformational characteristics of the short chains between the nodes in densely cross-linked networks. The dependence of the elasticity of the short chains on the elongation is stepped in character, and their conformational behaviour differs significantly from the generally adopted approximations of Langevin and Gauss[80].

In addition to the creation of the above statistical topological theory of the formation of polymer networks, work has continued on the development of traditional statistical methods for describing network polymers by means of the mathematical apparatus of the theory of branching processes[82-85]. In particular, a new parameter of the theory has been proposed—the probability of the termination of the chain of network development—whose magnitude determines not only the kinetics of the process of gel formation but also the topological structure and hence the properties of the cross-linked polymer in the highly elastic state; information on the structure of the gel can be obtained from the sol fraction of the polymer, which is easily analysed experimentally. When side reactions causing network growth to stop take place, the sol fraction contains the products of these reactions, including the monocyclisation reaction.

3. Supermolecular Structure

The next level of structural organisation of a polymer, reflecting the relative arrangement of its chain in space, must be characterised by the type of intermolecular interaction of the chains and their degree of ordered character. The first characteristic influences the magnitude of the free volume and the density of packing, which reveals itself in the morphological characteristics of the polymer[1,3,4,6].

Extensive systematic studies of the morphology of densely cross-linked (>10^{21} nodes cm^{-3}) epoxide polymers[1,3,4,6] have shown that the typical structural elements in these systems, which can be detected by electron microscopy, are globules. An important characteristic of these systems is that any attempts to change the nature of the globular structure by varying the chemical structure of the original epoxide oligomers and hardening agents, by changing the hardening conditions, or by the action of thermal and mechanical fields on the already formed network polymer did not lead to any significant change in the morphology of the system; in all cases it remained globular, and only the size of the globules changed.

These studies indicated that the fairly widespread view that globules are more highly cross-linked formations than the cross-linked polymer in the space between the globules is in general incorrect. Thus theories in which the variations in the mechanical properties of cross-linked polymers in the vitreous state are attributed to differences in the density of cross-linking of the globules cannot be correct.

The difference in the densities of the globules and the polymer in the space between the globules was extremely small, ~0.1%.[86] The physicomechanical characteristics of epoxide cross-linked polymers show extremely little sensitivity to the preliminary action of thermal, mechanical, and electromagnetic fields on the prepared polymer over a wide range of conditions. The variation in the properties of the polymers in this case does not exceed 20%. At the same time, even slight changes in chemical structure lead to fairly marked changes in the physicomechanical characteristics of the polymer.

These results are fundamental, since they show that the topological and supermolecular structures of the polymer, formed during the hardening process, are fixed by the three-dimensional network and cannot subsequently be changed by conformational rearrangement of the chains between the nodes without the rupture of chemical bonds.

The above observations led to the important conclusion that densely cross-linked polymers are characterised by a closer relationship between the different levels of their structural organisation, compared with linear polymers. The higher levels of the structure—topological and supermolecular—are determined to a considerable extent by the primary molecular structure of the polymer[1,3,6]. As a result, different external preliminary treatments of the prepared polymer, capable of producing radical changes in the properties of linear polymers, have a much less significant influence on the properties of densely cross-linked polymers, which to a large extent are determined by their molecular structure[87-98].

Studies of the density of epoxide polymers in the vitreous state have shown that the coefficient of molecular packing was unexpectedly high (K = 0.71–0.72), and appreciably higher than that for vitreous linear polymers[6,87,91]. This means, on the one hand, that the formation of chemical cross-linkages does not impose any kinetic restrictions on

the packing of the elements of the network, and on the other hand that the chains between the nodes, in spite of their considerable length (8–12 framework atoms), have a flexibility sufficient for closest packing to be produced. Subsequent experimental studies of the molecular mobility of epoxide polymers completely confirmed this conclusion.

Interesting and important results were obtained in an experimental and theoretical study of the kinetics and mechanism of the formation of the supermolecular structure of epoxide polymers[1,43,51,86].

An extremely general mechanism of the production of the supermolecular organisation of an amorphous polymer has been formulated, taking account of the kinetic characteristics of the process of its formation and its molecular mobility, and a mathematical model of the process has been developed. In this model, the size of the polymer cluster formed is greater, the greater the self-acceleration factor of the hardening process (irrespective of its specific mechanism) and the lower the molecular mobility of the polymer[98].

III. PHYSICOMECHANICAL AND RELAXATION PROPERTIES

Another important problem is the establishment of the relationship between the properties of cross-linked epoxide polymers in the vitreous state and the characteristic features of their structure. As indicated above, the equilibrium mechanical properties of cross-linked epoxide polymers in the rubber-like state is described completely by their topological structure and the conformation characteristics of the chains between the nodes. On going to the vitreous state, however, the situation changes radically[1,3–6,91,97]. The polymer matrices in high-strength composites are used at temperatures below the vitrification temperature, so that the study of the properties of epoxide polymers under these conditions is of particular interest; moreover, in general the properties of polymers in the vitreous state represent one of the least studied fields of polymer physics.

In view of the practical aspects of the application of polymer matrices, it is natural that the mechanical properties of these polymers were studied first. A cycle of studies carried out with epoxide cross-linked polymers with different chemical structures investigated the static and dynamic mechanical properties, the relaxation of stress, creep, various problems of the durability and breakdown and the relationship between these properties and the molecular and topological structures of the epoxide networks[1,3–6,71,87,88,94,96,99–107].

Study of the $\sigma-\varepsilon$ (elongation, compression, shear) diagrams has shown that in most epoxide polymers, in spite of the presence of a high concentration of chemical cross-linkages, at temperatures more than 100 K below T_g and moderate rates of deformation, plastic (induced–elastic) deformation is realised, and the frequently observed brittleness of specimens is due to their macroscopic defect character[1,3,6,91]. The limiting deformations at breakdown may be extremely high (10–15%). This conclusion is important, since it refutes the extremely widespread view that systems with such a high density of cross-linking cannot show plasticity.

Measurements of Young's modulus and the shear modulus, and also the yield limit, have shown that these important mechanical properties are practically independent of the topological characteristics of the network (the density of the nodes, the concentration of mono-rings[1,3,6,91,97]); only the strength was found to be sensitive to the concentration of mono-rings[1,3,95,97]. At the same time, as noted above, the mechanical properties of the networks in the highly elastic state are determined completely by their topological structure[1,6,8,60,61,78,79].

These results are fundamental, since they show that the properties of cross-linked polymers in the vitreous state must be related to the characteristic features of their packing[1,6,89,91,93,108], that is that the behaviour of networks, even when densely cross-linked, does not differ in this sense from that of linear polymers. The liquid–glass transition during the production of the network has a significant influence on the physicomechanical properties of the resulting polymer[91,97]. The slower the vitrification of the polymer during hardening (at low temperatures), the better its mechanical properties in the vitreous state, in spite of the lowered values of the degree of conversion at low hardening temperatures. At the same time, the values of the coefficient of molecular packing for specimens of a given polymer with appreciably different mechanical properties were found to be similar[91,97].

A possible explanation for these facts may be that the properties of a vitreous polymer are determined not only by the total fraction of the free volume in it but also by the nature of its distribution in the specimen. Direct measurements of the dependence of the free volume for epoxide systems on the concentration of chemical cross-linkages provides evidence in support of this suggestion[1,3,89,93,108].

The characteristics of the deformation and breakdown of epoxide polymers in the vitreous state have been studied[99–105]. In spite of the high density of chemical cross-linkages, in epoxide polymers, as in linear polymers, when a crack is propagated through the material, appreciable plastic deformations, irreversible under the given conditions, are observed in the opening of the developing crack. It is these deformations, preceding the rupture of chemical bonds, that to a large extent determine the stability of the material to the propagation of cracks, and hence its strength. These observations indicate that the extremely short bonds between the nodes in epoxide polymers are sufficiently flexible, and are able to undergo conformational rearrangements under deformation conditions.

The size of the plastic zone along the axis of elongation for films of densely cross-linked polymers (plane-stressed state) is equal to the thickness of the film, and this made it possible to formulate criteria for their breakdown[104].

The deformation of densely cross-linked polymers at values of the deformation close to or equal to the yield limit is accompanied by the rupture of chemical bonds[99–102]. This local breakdown of bonds during deformation long before the breakdown of the entire specimen is apparently due primarily to the short length of the chains between the nodes and the non-uniform distribution of stresses in the chains between the nodes. This mechanical degradation may be one explanation for the effect of the "anomalous" relaxational and deformational strengthening of densely cross-linked polymers, detected by various workers[3,99–102]. The essential feature of the phenomenon is that in contrast to linear polymers, during the successive relaxations of the stress or during deformation, the relaxation properties of the densely cross-linked polymers improve (the relaxation time decreases).

The practical result of the studies carried out was the development of epoxy-amine binding agents with record values of the modulus of elasticity (600–700 kg mm^{-2}) and yield limit (17 kg mm^{-2}) at room temperatures and ordinary rates of loading[3,6,91,96].

One of the most important characteristics of a binding agent is its heat resistance. A series of studies[1,3,6,34,35,89,91,109,110] established that the vitrification temperature T_g is determined unambiguously by the molecular and topological structures of the epoxide network. T_g for an epoxide polymer can be increased by high-temperature treatment (>150 °C) as the result of the reaction of unreacted (as a consequence of the topological limit) epoxide groups with

hydroxyl groups of the chains between the nodes[59]. This method of increasing the heat resistance of epoxide matrices for composites is hardly a promising technological technique, because the increase in the thermal stability and a definite but small increase in the value of the Young's modulus are accompanied by a marked increase in the brittleness of the polymer is also observed.

The unique relationship between the molecular structure of the network polymer and T_g makes it possible to use the method of increments to calculate *a priori* T_g for polymers with different chemical structures. This approach made it possible to propose and later to synthesise a number of highly heat-resistant epoxide binding agents.

The study of the vitrification temperature and mechanical behaviour of epoxide networks led to a non-trivial result of practical importance. It was found that important characteristics of the binding agents, such as the heat resistance and the mechanical properties, are determined by different structural parameters, in the first case by the chemical structure of the network, and in the second case by the packing of the chains in the polymer glass. This makes possible the directed and to some extent independent control of these properties of polymer binding agents.

The solution of these problems also made it possible to shed light on various general fundamental problems of the theory of the vitreous state of a substance. In particular, a fluctuational theory of vitrification[111] and a diffusion model of the volume relaxation of glasses have been developed. It was proved experimentaly for the first time[112] that the relaxation of the free volume in polymer glasses takes place not only by a local elasticity mechanism but also by a diffusion mechanism, which is revealed in two new non-trivial effects: the scale effect of the density of epoxide films and the scale effect of their rate of annealing.

A new effect, not yet understood, has also been detected, namely that the relaxation of the free volume in polymer glasses, taking place by a diffusion mechanism, is accompanied by ordering of the structure of the surface layers of the polymer[113].

Important information on the structure of network epoxide polymer glasses has been obtained in studies of their molecular mobility[1,3,6,64,87-95,106,108-110,114-123]. The use of a wide range of methods—mechanical and dielectric relaxation, dilatometry, thermally stimulated depolarisation, NMR, EPR, and calorimetry—established that in densely cross-linked epoxide polymers there is the entire spectrum of molecular movements characteristic of linear polymers. At the same time the molecular movements in these systems are characterised by a number of important features[1,3,6,89,90,92,109,110,114,119]:

1) the chemical units of the epoxide networks (their type and concentration) have no significant influence on the kinetic parameters of the local movements of all types;

2) the half-widths of the α-transitions in cross-linked polymers are usually much smaller than those in linear polymers;

3) the activation energy of the segmental mobility is always lower than that for linear polymers, and decreases with increase in the density of the cross-linkages, whereas the vitrification temperature increases.

The last two facts indicate on the one hand that there is a more uniform distribution of the segments with respect to length in a cross-linked polymer, and on the other hand that they are less extensive than the segments of linear polymers. Direct experimental measurements confirmed this conclusion, and showed that the segment in a network formed from individual diepoxides and diamines is a chain between two neighbouring chemical units[123].

IV. THE MODIFICATION OF EPOXIDE BINDING AGENTS

One of the traditional methods for producing a directed change in the properties of binding agents is by their chemical and physical modification. A series of studies[3,6,71,88,94,95,106,107,110-121,124-129] investigated the physicomechanical and relaxational properties of epoxide compositions over a wide range of chemical structures of the epoxide oligomers and hardening agents. Studies have been made of the properties of epoxide compositions whose chemical structure had been changed in directed fashion by carrying out copolycondensation reactions or by simultaneously carrying out reactions in the hardening system involving the polycondensation and polymerisation of a monomer or monomers of different kinds, or by other methods. Particular attention was paid to the study of the physicochemical modification of epoxide binding agents by the addition of low-molecular-weight rubbers[3,107,124-128]. This method made it possible to increase by almost two orders of magnitude the value of the effective surface energy of breakdown of the epoxide binding agents; this is extremely important for increasing their resistance to impact[107]. Extensive thermodynamic and kinetic studies of the production of the phase structure of epoxide polymers with inclusions of rubbers of different chemical character are making it possible to approach an understanding of the relationship between the chemical nature of the components and the conditions of the preparation of compositions and the phase structure of the composition material.

The phase equilibrium in the original epoxide–rubber systems is described satisfactorily by the Flory–Huggins theory[128]. A thermodynamic analysis of the change in the phase state of hardening epoxide–rubber systems showed that during hardening, the thermodynamic affinity between the epoxide polymer and the rubber decreases, leading finally to the exhaustion of their mutual solubility.

The kinetic condition of the production of the phase structure of epoxide–rubber compositions are determined by the ratios of the rates of the chemical reaction of hardening and the mutual diffusion of the components[124-128]. On the basis of these studies, ideas were developed about the mechanism of the production of the phase structure of epoxide–rubber compositions, a characteristic feature of which is the growth of the nuclei of the new phase under conditions of constantly changing coefficients of mutual diffusion of the components. The ideas developed make it possible to explain why the original thermodynamic compatibility of the components and the width of the distribution of the particles of the dispersed rubber phase with respect to size change in the opposite sense. They also make it possible to understand the frequently observed polymodal distribution of the particles of the dispersed phase with respect to size.

The proposed[124-128] model of the production of the phase structure is apparently of general value for any dispersed-reinforced polymer compositions, whose formation is related to the phase separation of the initially homo-phase mixture of the original components, and makes it possible to influence their phase structure, and hence their useful properties, in directed fashion.

V. CHARACTERISTIC FEATURES OF THE STRUCTURE AND PROPERTIES OF EPOXIDE POLYMERS AT THE BOUNDARY WITH A SOLID SURFACE

The relationship between the physicomechanical properties of epoxide binding agents in the vitreous and rubber-like states and the different levels of their structural organisation was examined above. The processes involved in the

hardening of binding agents in a composite material, however, often taken place in thin layers, in close contact with the filler surface. A large number of studies have shown that a filler may have a significant influence on a matrix, and so-called "boundary layers" are formed in it, with properties different from those of the block polymers[131,132]. The production of these boundary layers is usually attributed to the chemical influence of the solid surface of the filler on the production of the binding agent, the selective sorption of the components of the reaction system, the orienting influence of the surface on the molecules of the reagent and reaction product, etc. The large thickness of the boundary layers (up to tens and even hundreds of microns), however, can hardly be explained in terms of existing thermodynamic concepts.

Published data on this topic are extremely contradictory, apparently because there are kinetic factors, not previously taken into account, which are decisive in determining the observed changes in the properties of the matrix formed on the solid surface.

Various model experiments[133-136] have indicated that this decisive factor may be the internal stresses produced directly during the formation (hardening) of the polymer matrix in the composite. The internal stresses (shrinkage and thermal) arise unavoidably during the hardening of the binding agent in the composite. An important role in the production of composite materials may be played by other sources of internal stresses: 1) stresses produced by the relaxation of the volume of the previously deformed filler, and 2) stresses produced by a change in volume as a result of a phase transformation in the filler. The last two types of stress are easily modelled. Thus the appropriate experiments have been extremely informative from the viewpoint of the determination of the role of internal stresses in the production of composite materials with an epoxide matrix.

Studies involving the extensive use of various relaxation methods and the photoelasticity method have made it possible to investigate the kinetics of the production of internal stresses, their spatial distribution close to the boundary of an inclusion, the gradient of properties (T_g) of the matrix close to an inclusion, and the influence on these parameters of the nature of the adhesion interaction between the matrix and an inclusion, the conditions of hardening, and other factors. A distinct correlation has been noted between the observed gradient of the properties of a matrix at a previously deformed inclusion and the gradient of the developing stresses. Analogous results have been obtained in other model experiments. These data indicate a clearly defined causal relationship between the changes in the properties of a matrix formed on a solid surface and the internal stresses produced.

In addition to the decrease in T_g of a polymer produced in a field of mechanical forces, this polymer also shows an increase in the proportion of the sol fraction, a decrease in the equilibrium modulus of high elasticity, and the production in the specimen of structural stresses, that is residual stresses which are not annealed under any conditions. All these changes in the matrix are greater, the greater the stresses operating in the hardening process.

The observed changes in the properties of the matrix can readily be understood if it is assumed that the process of hardening of the matrix is accompanied by mechanodegradation of the chains of the network[134,135]. The data obtained lead to the following picture of the processes involved in the mechanodegradation of hardening polymer systems under the influence of mechanical stresses. In the range of pre-critical degrees of transformation, when the hardening system remains liquid and has a low viscosity, the applied stress relaxes. In the range of gel formation, when the viscosity of the system increases sharply, the rate of relaxation decreases, and although the stresses operating are extremely weak, they may nevertheless be comparable with the destructive stresses, since the number of elastically active chains, that is chains "holding" the load, in the network in the range of gel formation is also small, and the strength of this system is low. After the point of gel formation, the number of elastically active chains and hence the strength of the polymer increase sharply, and the system can now withstand a load (external or internal) without breakdown.

Thus during the formation of a cross-linked polymer there is a narrow range of degrees of transformation, close to the point of gel formation, in which the cross-linked polymer is very vulnerable to mechanical loads. The degree of damage to the polymer evidently depends on the level of stresses operating and on the kinetics of the hardening process, which determine the time for which the forming polymer is in the "danger" zone.

Although the qualitative picture appears quite satisfactory, quantitative agreement is not observed. Calculations show that the number of degraded chains between the nodes, required to explain the observed changes in the vitrification temperature of the polymer, is one hundred times that determined experimentally by the inhibitor method. Additional studies are therefore necessary to reach a final conclusion about the mechanism of the influence of internal stresses on the structure and properties of polymer matrices in a composite.

Nevertheless, it has already become clear that it is kinetic factors (the nature of the production and relaxation of internal stresses and the excess free volume) that are decisive in determining the observed changes in the properties of polymer matrices produced in contact with a solid surface. An understanding of these regular features is extremely important for the directed control of the properties of composite materials.

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To summarise this extensive cycle of studies, it can be stated that they essentially form the basis of a branch of the physical chemistry of macromolecular compounds which is of practical importance but which has not been developed theoretically, namely the field of densely cross-linked polymer systems.

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Institute of Chemical Physics,
Academy of Sciences of the USSR,
Moscow

Translated from *Uspekhi Khimii*, 53, 290-308 (1984) U.D.C. 678.5-419.8,536.4

High-strength and High-modulus Reinforced Plastics

E.S.Zelenskii

Studies of the formation, structure, deformation, and fracture of polymeric composite materials reinforced with long fibres are reviewed. The main factors which determine the strength and the elastic modulus of reinforced plastics under short-term static load are discussed.
The bibliography contains 110 references.

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I. INTRODUCTION

Plastics reinforced with an oriented array of long, high-strength, and high-modulus fibres are a new class of polymeric composite materials characterised by a marked anisotropy in physico-mechanical properties, depending on the type of fibres used, their mutual orientation, and the relative content of fibres in the matrix.

Because of the ease of controlling (between wide limits) the strength and the deformability of these materials, as well as some of their physicochemical properties (density, resistance to chemicals and to water, thermal and electrical conductivity, etc.), reinforced plastics can be used as constructional materials for a variety of applications, including highly stressed units and components.

We shall not attempt to discuss the structure, properties, and special features of reinforced plastics of various types, which have been recently reviewed in both Soviet and foreign publications[1-7], and we shall only examine the problems of retaining (or exploiting) the strength and the elastic modulus of the fibres in an oriented layer of reinforced plastic stressed in the direction of the fibres.

It is important to define correctly the initial characteristics of the strength members, i.e. the characteristics of the fibres when first prepared. The direct measurement of the properties of the fibre is complicated by the danger of damaging the sample (mechanically or physicochemically), thus degrading its properties while preparing the measurement samples[8]. These difficulties are most marked in the determination of the strength of the fibres, since in this case the measurements are affected not only by the sample preparation conditions but also by the scale factor, by the strain rate, and by the method of clamping the sample in the tensile tester. The measurement of the elastic modulus is usually straightforward, but in the case of organic fibres it may be influenced by several factors.

With oriented samples carefully prepared under laboratory conditions several workers have obtained characteristics corresponding to the initial properties of the fibres. This success makes it even more important to develop methods of quantitative analysis of the influence of various structural defects in real reinforced plastics on the mechanical properties of the components made from them.

Information on the adhesive strength of the fibre–polymeric matrix system is essential in studies of interactions in this system. Special models have been developed to calculate the adhesive strength, to identify the special features in the formation of the adhesion couple, and to give a quantitative formulation of the effect of the adhesive strength on the behaviour of the plastic under different stress conditions.

In addition to a strong adhesion the polymer matrix should offer a set of elastic and mechanical characteristics which ensures a uniform distribution of the stress over the system of fibres experiencing deformation under load. Theoretical work on this problem has been published both in the Soviet Union and abroad[9-12]. The use of epoxy polymer matrices in composite materials is reviewed by Rozenberg and Oleinik in the present issue of this Journal (see p.164).

The strength and elastic modulus of an oriented material under axially symmetrical load can be increased by increasing the relative content of reinforcing fibres. Therefore one of the problems in the design of reinforced plastics is the production of systems having a high packing density, with a regular hexagonal packing (in the case of fibres with a circular cross-section) and a minimum number of defects.

The materials known as hybrid polymer composites have attracted much attention during the past ten years. By combining within the same composite two or more types of fibre, or more than one matrix, we are able to control the properties of reinforced plastics between much wider limits, and in some cases we can achieve synergetic effects. It is also possible to vary the properties of the material in a prescribed way in the bulk across the cross-section of the item.

Another important area of research is concerned with the phenomena associated with the frontal or the uniform solidification of polymers and composite materials. Studies of stressed and strained states created during the formation, cooling, and storage of the material and of the residual stresses and strains (after relaxation) should lead to improved technological processes for the production of components from reinforced composite materials having the required properties.

We shall not attempt in this review to survey the whole of the current work on the development of high-strength reinforced plastics and on studies of their deformation and fracture and of their behaviour under practical conditions. The discussion will be confined mainly to the aspects developed by Enikolopov and his co-workers.

II. REINFORCED PLASTICS WITH AN ORIENTED STRUCTURE

1. Effect of the Strength and Length Distribution of the Elementary Fibres and Filaments on the Strength of Oriented Reinforced Plastics

One of the main problems in the study of the tensile strength of oriented composite materials is the determination of the initial strength of the fibres. Existing models of fibre structures can be used to calculate the elastic modulus

but are almost useless for predicting the strength characteristics of fibres[13].

The effect of the scale factor on the strength of elementary organic fibres (Vniivlon, Kevlar-49, Terlon) has been studied[14], and it was found that their strength characteristics are adequately described by the statistical theory of strength with a distribution function whose parameters are determined by the structure of the fibre. For Kevlar-49 and Terlon the strength distribution histogram was bimodal, due to the presence of various types of defect associated with the amorphous–crystalline structure of polymers showing a "shish-kebab" morphology[15].

The theory of the strength of a bundle of unattached fibres has been discussed[16] by assuming a Weybull distribution of fibre strengths. The high-grade physico-mechanical characteristics of reinforced plastics are the result of the simultaneous deformation of high-strength fibres interconnected by the polymeric binder. According to the statistical theory of fracture proposed by Rosen[11] the strength of an oriented composite material is equal to that of a bundle of non-interacting fibres of appropriate length (called the ineffective length, l_{ineff}). Experimental studies of the dependence of the strength of the bundle on the scale factor and comparisons with the strength of microscopic samples of plastic based on single fibres or braids (small bundles of fibres connected by the polymeric binder) have confirmed that the strength of a micro-plastic is the same as that of a bundle of unattached fibres of length l_{ineff}. This length can be calculated from the relative hardness of the components (according to Rosen) or from data on the adhesive strength in the fibre–polymer matrix system[17].

However, studies of reinforced plastics have brought to light a number of factors which are incompatible with Rosen's theory: 1) the dispersion of the strength of the fibres and of the micro-plastics is approximately an order of magnitude greater than the calculated value[14]; 2) the strength of the micro-plastics is dependent (albeit slightly) on the length of the sample, and falls off markedly when the standard ring specimen is replaced by real mechanical components and mass-produced items. These discrepancies are due to inhomogeneities and defects in the structure of real materials which are ignored in Rosen's idealised model. Among the most important of these effects is the instability of the properties of the fibres used, for example, in the windings of reinforced plastics.

Detailed studies have been made of the properties of filaments based on organic fibres: the scatter of the elastic moduli was relatively slight (variation coefficient $\nu_E \approx 4\%$), but the strength of the individual fibres within a braid covered a range of 20–25%, with a variation coefficient of 6–12% (depending on the length of the sample). The dispersion of the Weybull parameter β, which describes the effect of the scale factor, was also found to be relatively large[16].

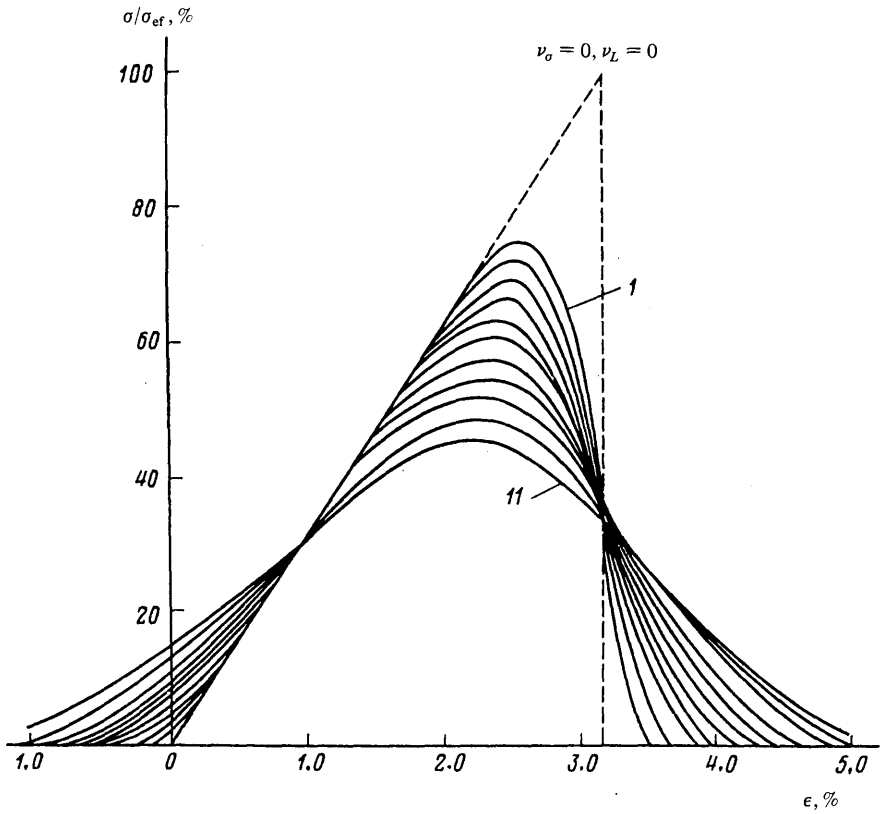


Figure 1. Tensile diagrams ($\sigma/\sigma_{ef}-\varepsilon$) calculated for bundles of organic fibres with different length dispersion: curves *1–11* correspond to variation coefficient of length (ν_L) between 0 and 1% in steps of 0.1%; σ is the strength of the bundle, σ_{ef} is the mean strength of the elementary fibre[18].

The interaction between the elementary fibres in the filaments, resulting from their partial adhesion during the production of the filament or from the twist in the filament, can be described by an appropriate ineffective length (for organic filaments, 20–150 mm), or alternatively by the ratio of the Weybull coefficients for the filament and for the elementary fibre respectively ($\beta_f/\beta_{ef} = 1.3–2.0$). The interaction between the fibres resulting from the presence of the polymer matrix causes l_{ineff} to decrease and β_f/β_{ef} to increase. For a micro-plastic based on Vniivlon filaments and an epoxy polymer matrix $l_{ineff} = 0.1–0.3$ and $\beta_{mp}/\beta_{ef} = 10–20$.

The $\sigma-\varepsilon$ tensile diagrams of the filaments for loads near the maximum for each sample usually include a non-linear region (due to a gradually increasing number of broken fibres, which produces a decrease in the aggregate cross-section of unbroken fibres). Micro-plastics under load break almost instantaneously, and a non-linear portion is not observed in the $\sigma-\varepsilon$ diagram, i.e. their behaviour under load is the same as that of elementary fibres.

However, because of the dispersion in the strength of the filaments themselves, which produces a dispersion in the strength of the resulting micro-plastics, a real reinforced plastic (for example, the ring samples with a uniform orientation) can be treated as a bundle of micro-plastics having different strengths. The breaking of one member of such a system creates a large-scale defect (a stress concentrator), which weakens the structure more markedly than the breaking of an individual fibre. This is one reason for the failure to exploit the initial strength of the elementary fibres in real reinforced plastics (as opposed to micro-plastics).

Another important contribution to the sequential breaking of the elementary fibres in real materials is the dispersion of the length of the fibres in filaments and in braids. Length inequality of the fibres in filaments occurs even at the fibre production stage, due to chemical and thermal fluctuations in the reaction region; dispersion of the length of fibres in braids occurs in the textile filament production processes (spinning and twisting), and also on the reeling machine.

A mathematical model[18] of the breaking of fibre bundles (filaments, or braids) which allows for the dispersion of the fibre length in terms of the variation coefficient ν_L has recently been proposed. The $\sigma-\varepsilon$ tensile diagrams calculated for braids in which ν_L varies from 0 to 1% are shown in Fig.1, and the dependence of the breaking stress of the braids on the parameter ν_L is shown in Fig.2. The broken lines are the tensile diagram for a single fibre or for a bundle with $\nu_\sigma = 0$ and $\nu_L = 0$.

The dispersion of the length of filaments in braids is usually studied by direct measurement of the filament lengths. No attempt is made to measure the dispersion of the fibre length within the filament. A method of measuring both the dispersion of the fibre length in the filaments and the overall dispersion of the fibre length in the braids was proposed in Ref.18. It relies on an analysis of the non-linear part of the $\sigma-\varepsilon$ tensile diagram for a filament, on the assumption that the non-linearity is due to the sequential involvement of the fibres in the deformation of the filament. The fractional number of fibres under load at a given deformation of the filament can be determined by comparing the measured stress of the filament with the stress calculated by Hooke's law. Differentiating the $\sigma = F(\varepsilon)$ dependence with respect to deformation gives the fibre length distribution curve and the variation coefficient ν_L.

Within a single filament the dispersion of the strength of organic fibres (ν_L) is usually found to be less than 0.12%, and for braids of these filaments it increases to 0.15–0.25%, which can lower the strength of a bundle (or braid) of these filaments by approximately 10% (see Fig.2); an analogous decrease was found in studies of the strength of micro-plastics based on braids in which the length dispersion was artificially modelled by previously applying different loads to the braid. When the problem is put in the elastic formulation a given dispersion of the stress is equivalent to a dispersion of the length of the filaments in the braid: experimental studies of the effect of the modelled dispersion of filament length in braids on the strength of the micro-plastics prepared from them agree very well with calculations (see Fig.2).

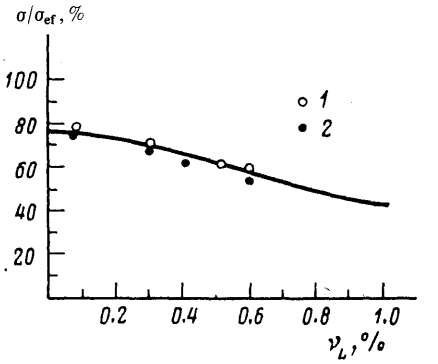


Figure 2. Reduced strength of the bundle of fibres σ/σ_{ef} against the variation coefficient of the length of fibres ν_L; the curve shows the theoretical dependence for a bundle of unattached organic fibres; the experimental points were obtained in tests on bundles or braids (*1*) and on micro-plastics (*2*).[18]

We note that the adverse effect of the dispersion of the length of fibres in filaments or in braids on the strength of reinforced plastics can be most marked in materials based on carbon or boron fibres, whose breaking strain is often less than 1%.[1]

2. Interaction of the Polymer Matrix with the Surface of the Reinforcing Fibres and Effect of the Adhesive Strength on the Mechanical Characteristics of Reinforced Plastics

The properties of composite materials depend not only on those of the components (fibres and matrix) but also on the interactions between the components, and especially on the strength of adhesion at the interface, which determines the effectiveness of the transmission of stresses through the phase boundary.

In spite of the obvious importance of studies of the adhesive strength in the development of reinforced plastics little was known for a long time on the changes in adhesive strength at the fibre–polymer interface: studies of adhesion have been traditionally confined to large-scale samples (prisms, plates, etc.). It was not clear to what extent the results obtained for flat surfaces could be transferred to cylindrical surfaces 10–100 μm in diameter (i.e. in the range of diameters of the fibres used in reinforced plastics). We should also note that for most of the high-strength reinforcing fillers used at present (carbon, organic, boron) the direct measurement of the adhesive strength in the fibre–polymer system is the only way of assessing the strength of

the coupling, since large test samples (plates, prisms, etc.) with the same fibre area cannot be prepared.

The apparatus and procedures which have been developed for preparing polymer–fibre composite samples, the adhesion testers for studying these samples at temperatures between −195 and +200 °C at different loading rates and in different atmospheres, and the new methods of treating the results of experiments on competitive (adhesional and cohesional) breaking processes have allowed the dependence of the adhesive strength in the fibre–polymer system on various factors to be studied systematically. The factors include the cooling and storage conditions, the measurement temperature, the rate of application of the stress, the composition of the binder, the type of fibre, the treatment of the fibre surface, etc.[18–34].

The most characteristic feature of adhesion couples is clearly seen in polymer–fibre systems: a non-uniform distribution of stresses at the interface, resulting from differences in the physico-mechanical characteristics of the components. This produces a strong dependence of the measured adhesion strength on the shape and size of the sample, and we must define the criteria for the most rational choice of numerical values of the adhesion strength. The local adhesion strength τ_{loc} has been proposed as the characteristic least sensitive to geometric factors: this parameter is determined by extrapolating the experimental results to zero length of the adhesion couple[26]. The τ_{loc} value can be used as a measure of the interaction at the interface, and also in studies of the nature of the adhesion and of the mechanism of the adhesion failure[27,28].

Studies of the dependence of the local adhesion strength of epoxy polymers on temperature and hardening rate have shown that under isothermal conditions τ_{loc} varies with the degree of hardening in the same sense as the hardness of the binder, tending towards an asymptotic value[27]. From studies of the kinetics of the development of adhesional strength during hardening it was found that the adhesion of these binders to steel and boron fibres is mainly due to chemical bonds[27].

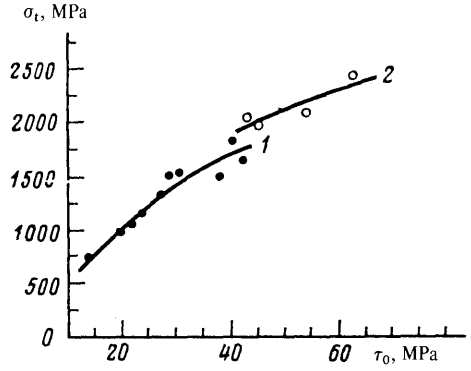


Figure 3. Dependence of the tensile strength of singly oriented glass fibre composites on the adhesion strength of the appropriate polymer–fibre system: *1*) for alkali-free glass fibres, *2*) for fibres of VMP grade[33].

Work on the dependence of the adhesive strength of polymer–fibre systems on temperature and loading rate has shown that below the glass transition region of the adhesive the local adhesive strength falls off linearly with increase of temperature and increases linearly with the logarithm of the loading rate[28–30]. This suggests that the adhesive failure of components (like their cohesive failure) takes place by a thermal fluctuation mechanism.

Refs.28, 31, and 32 describe a quantitative study of the relationship between the adhesive strength and the strength of the sample under tensile stress, compression, bending, and shear. The parameter used as a measure of the adhesive strength in this work was the quantity τ_0, defined for the final length of the sample, since it is affected by all the forces acting on the elementary cell of the reinforced plastic and therefore it can reflect more accurately than τ_{loc} the conditions of adhesion failure at the interface in real composites.

In oriented glass fibre composites prepared from various binders the tensile strength of the material σ_t increases with the adhesion of the binder to the fibre (see Fig.3). At high values of the adhesive strength we note a tendency for the plot of σ_t against τ_0 to reach a saturation level.

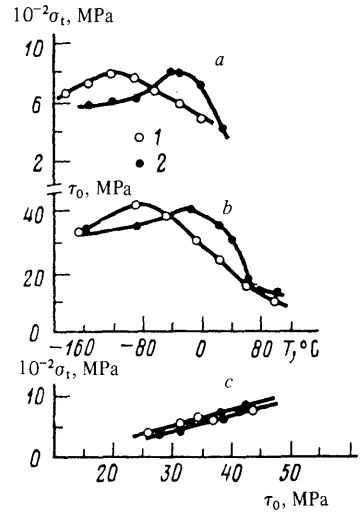


Figure 4. Effect of temperature on (*a*) the tensile strength σ_t of uniformly oriented glass fibre composites and (*b*) the adhesion strength τ_0 of the polymer–fibre system; (*c*) are the correlation curves; the binder is *1*) butvar-phenol, *2*) epoxy-phenol.

Changes in the same sense of the adhesive strength τ_0 and of the strength of the glass fibre composite σ_t are observed also in studies of temperature effects (Fig.4). Since both the strength of the glass filaments and the strength of the binder increase monotonically as the temperature T decreases, the observed correlation between the shape of the σ_t–T and τ_0–T curves suggests that in these composites the weakest member is the phase boundary, and therefore that the fracture of these materials begins at this boundary.

The most meaningful information on the relationship between the adhesion at the interface and the properties of the material is obtained from experiments in which the fibre and the binder material are kept constant, but the adhesion is varied by modifying the surface of the fibrous filler. Work of this type has shown[31,32] that changes in the adhesive interaction are accompanied by corresponding

changes in the strength of composites with a single orientation (both pressed and wound). The changes are in the same sense for all types of test (in tension, shear, compression, and bending, see Fig.5).

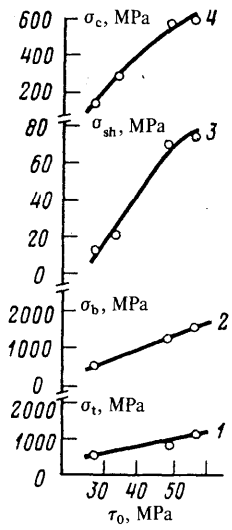


Figure 5. Strength of uniformly oriented glass fibre composites prepared from fibres with a pristine or a modified surface against the adhesion strength; EDT-10 binder, *1*) tension, *2*) bending, *3*) shear, *4*) compression[32].

Thus recent work shows that in glass fibre composites the adhesive strength of the polymer–fibre system is one of the factors mainly responsible for the mechanical characteristics of the material. The fracture of these materials (under tensile load) also reflects the level of adhesion at the interface: we observe a transition from failure at the interface (for small values of τ_0) to fracture by the increase in the number of broken fibres (for large values of τ_0). In the latter case the statistical model of fracture proposed by Rosen is applicable to the glass fibre composite.

In high-strength composites based on organic fibres of the Vniivlon type no correlation is observed between the adhesive strength and the strength of the material: for all the binders examined (covering a range of τ_0 from 40 to 60 MPa) the strength of the material under tension, compression, bending, and shear remained constant. This suggests a fracture mechanism controlled by the weak bond between the fibrils of which the fibre is composed[1].

In glass fibre composites (based on existing binders) a search for methods of modifying the glass surface so as to improve the adhesive strength should yield reinforced materials with enhanced mechanical properties.

In organic fibre composites based on highly oriented fibres of the Vniivlon type surface treatment aimed at strengthening the interaction of the fibre with the binder cannot by itself improve the physico-mechanical properties of the composite, and we must seek to modify the structure so as to enhance the transverse strength of the fibres under tension, i.e. to strengthen the bond between the fibrils.

3. Reinforced Plastics with a High Relative Content of Fibres

One method of raising the strength and the elastic modulus of reinforced plastics is to increase the relative content (by volume) of high-modulus and high-strength fibres, i.e. the reinforcement coefficient K_a. Traditional winding methods give materials containing only 65–70 vol.% of fibres, as compared to the theoretical K_a value of 90.7% for hexagonal close packing of fibres of equal diameter.

Various workers have reported a maximum on the plots of the physico-mechanical properties of reinforced plastics against the relative fibre content, usually in the region of 60–65%.[3,35] We can attribute the decrease in strength of the plastic at high fibre contents to an increase in the porosity of the samples and to the difficulty of producing uniformly thin (less than 1 μm) and yet continuous layers of the polymeric matrix. An indirect confirmation of this conclusion comes from the reported shift of the maximum towards higher values of K_a when the fibre diameter is increased[36].

The technological difficulties which prevent the incorporation of a high density of fine fibres are due mainly to the friction between the fibres during the formation of the material, which opposes their redistribution into the optimal hexagonal configuration. Furthermore, the dispersion of the fibre diameters lowers the theoretical limit of packing density (except for some special relationships between average fibre diameters in the case of a bimodal distribution).

To overcome these difficultes we must first of all optimise the structural order of the reeled element consisting of filaments or braids, i.e. create a close packing at the stage preceding the fixing of the positions of the filaments. Equally important is the achievement of a uniform distribution of the polymeric binder between the fibres[37]. This is done by repeated steeping of the filaments and braids in the binder during the winding of oriented reinforced plastics, by stretching them by friction (without slippage) on tensioning pulleys, and by forming an ordered, thin tape from a number of filaments or braids in a special profiling stacker. Some workers have applied ultrasonic vibrations to the stacker in order to lower the friction and to achieve a closer packing of the filaments in the tape, as well as a uniform penetration of the binder into the fibrous material. These new technological processes have given ring samples of glass or organic fibre composites in a single orientation containing up to 85 vol.% of fibres, i.e. approaching the theoretical limit, coupled with a negligibly small porosity of the samples (less than 1%).

When thermoplastic organic fibres are used the fibre content of the reinforced composite can be as high as 90 to 100 vol.%.[38,39] These high packing densities are achieved through irreversible thermal deformation of the fibres normally to their axis, which changes the fibre cross-section from a circular to an arbitrary shape, imposed by the contact with the neighbouring fibres. To prepare these maximally reinforced organic fibre composites the technological parameters must be chosen so as to retain as far as possible the initial strength and stiffness of the fibres in spite of their thermal deformation. A strong bond between the profiled fibres can be obtained from the self-adhesion forces (by direct interaction of the fibres) or by interposing thin layers of binder between the fibres.

If the porosity is kept to a minimum (less than 1%) the elastic modulus E and the tensile strength of the samples show a linear increase (as required by the additivity principle) up to the highest volume contents of fibres of different types. These results are illustrated (Fig.6) by plots (in relative units) of the characteristics of glass fibre reinforced plastics based on fibres 9–11 μm in diameter and an epoxy-diane binder. Increasing the fibre content of the glass fibre

composites increases their strength under compression more markedly than under tension: this is explained by the specific effect of the close-packed array of fibres, which prevents the loss of strength.

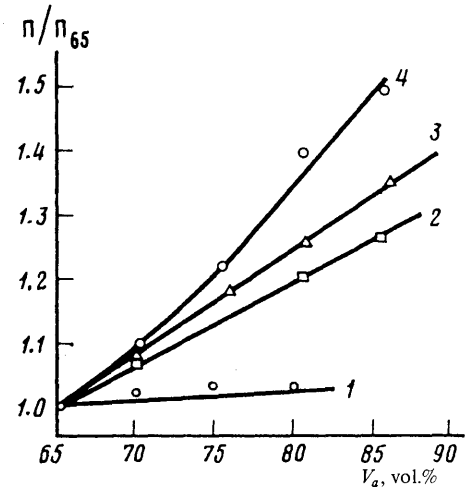


Figure 6. Effect of the fibre content by volume on the physico-mechanical characteristics of glass reinforced composites; П is a characteristic of the glass fibre composite for any value of the fibre content V_a, $П_{65}$ is the same characteristic for a 65% fibre content, *1*) τ_{sh}, *2*) σ_t, *3*) *E*, *4*) σ_c.[37]

4. Hybrid Polymeric Composite Materials

The preparation of hybrid polymeric composite materials (HPCM) by combining two or more types of reinforcing fibre (glass, organic, carbon, or boron) is a promising area of research in materials science, because of the prospect of controlling the properties of these materials between much wider limits.

The most important influence on the physico-mechanical behaviour of HPCM (especially under tension) is from the difference in the limiting deformations of the fibres present in the material. Organic–glass and carbon–boron plastics have been studied as HPCM based on fibres with similar deformation characteristics. The physico-mechanical properties of these materials are exactly described by the additivity principle.

An entirely different behaviour is observed in studies of HPCM containing fibres with substantially different deformation properties. In HPCM with alternate reinforcing elements having a low linear density or with alternate layers less than 0.1 mm thick the different fibres in carbon–organic, carbon–glass, boron–glass, and boron–organic composites do not break simultaneously under tension. Fig.7 shows as an example the tensile diagrams of carbon–glass composites with different ratios of carbon to glass fibres. In the initial region *I* (Fig.7) the carbon and the glass fibres are being deformed together. At a relative deformation of 0.7–1.0% we observe the fracture of samples containing more than the critical amount of carbon fibres (25 vol.%, curves *1* and *2*). At lower contents of carbon fibres this deformation does not cause breaking. In region *II* (Fig.7) curves *4* and *5* are non-linear, indicating the gradual breaking of the long carbon fibres into progressively shorter lengths. The presence of a "quasi-plastic" region (*II*) in the tensile diagram of the HPCM gives an increased breakdown energy, impact strength, and fatigue and dynamic strength in these materials. Beyond this region the almost linear region *III* extends up to the limiting deformation of 3–4%. On increasing the content of glass fibres the deformation at break of the carbon fibres in carbon–glass composites increases from 0.7 to 1.5%. This synergistic effect is apparently due to the repeated breaking of the carbon fibres into progressively shorter pieces, and to the avoidance of macroscopic cracks and premature failure of the material in glass fibre composites.

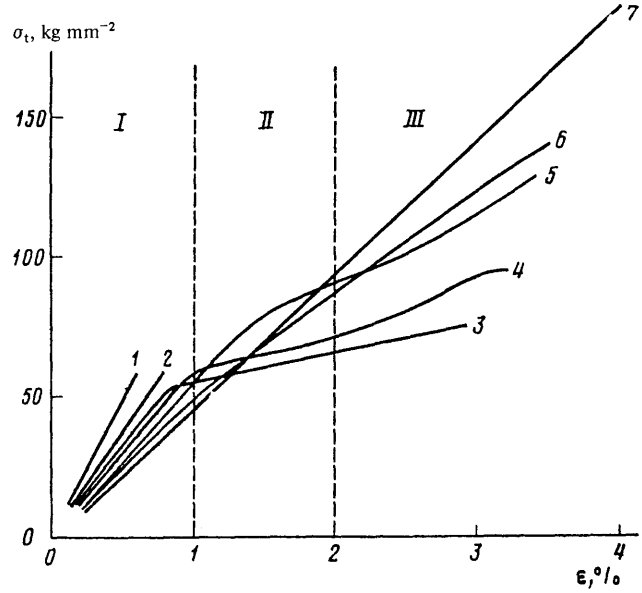


Figure 7. Tensile diagrams for uniformly oriented ring samples of carbon and glass fibre composites with different ratios by volume of carbon and glass fibre contents (%): *1*) 100:0, *2*) 78:22, *3*) 58:42, *4*) 41:59, *5*) 26:74, *6*) 12:88, *7*) 0:100.[52]

Under compression the dependence of the strength on the content of fibres with different elastic moduli is almost linear in HPCM. The elastic modulus stays linear after repeated (up to 10 times) load applications. This means that the carbon and the organic fibres when present in a matrix of glass and boron fibre composites can retain their strength at deformations (and therefore also at stresses) 2–3 times greater than in the simple carbon and organic fibre composites. These synergetic effects allow us to increase the elastic modulus of glass or organic fibre composites by small additions of carbon fibres, and to increase the compressive strength of carbon fibre composites by combining carbon and glass fibres.

An interesting possibility in the development of HPCM is the production of components with variable properties by varying the relative amount of different fibres in different parts of the article. This feature should allow us to control

the stress field in mechanical components both during assembly and in service. It should also be possible to solve the inverse of the traditional problem, i.e. given the most favourable stress field in the component, determine the required material structure. The effectiveness of this approach has been demonstrated for thick-walled vessels under external or internal pressure. Hybrid composite materials have attracted a great deal of interest in both the Soviet and the foreign scientific literature[40-48], but the reported experimental results are not always easy to compare because of the failure on the part of authors to quote the parameters of the material structure, the extent to which the components are kept discrete in the hybrid material, and the relative configuration of the reinforcing elements. The results reported by Phillips[46,47] appear to be the closest to ours[44,45].

We should note that although the theory of the construction and of the behaviour of hybrid composites is still in its early stages these materials have already been widely used in practical applications ranging from aviation components to sports equipment[48].

III. DEFORMATION AND FRACTURE OF MATERIALS WITH COMPLEX REINFORCEMENT

Recent component designs rely on multi-layer polymeric composite materials (PCM) with different and often complex patterns for the orientation of the reinforcing elements. The choice of reinforcement, of binder, and of orientations is determined by the function of the component and by its conditions of service. Materials having identical reinforcing elements and binders and differing only in the pattern of the reinforcement are entirely different materials as regards their mechanical properties. We therefore need theoretical models of the PCM to predict their behaviour with different orientation schemes of the reinforcement from a minimum of experimental information.

Studies of this type have been reported for glass, carbon, and organic fibre composites prepared by the winding method and for hybrid materials based on glass and carbon fibres[49-66].

Tube samples are used for experimental studies of the mechanical behaviour of materials produced by the winding method with complex reinforcement patterns. Special test methods had to be developed for tubular PCM samples under different loading conditions[49,61-63], because there are no standard test methods for this sample geometry.

Purely phenomenological studies of strength as a function of the angle of the reinforcement[57] have shown that in both carbon and glass composites the shear strength can be described by a formula which follows from the Gol'denblat–Kopnov strength criterion. Hence the calculation requires a knowledge of three experimental values of the torsional strength for three known winding angles[64].

A simpler dependence of the strength on the reinforcement angle was obtained[56] from a different phenomenological criterion, which allows for the structure of the material by formulating the failure condition for the plane where fracture is most likely. This criterion gave formulae for the dependence of the strength under uniaxial extension and of the torsional strength on the reinforcement angle in terms of the strength observed experimentally (under the same loading conditions) for a single, arbitrarily chosen winding angle. These theoretical formulae are satisfactorily consistent with experimental curves for glass and carbon fibre composites with winding angles of $\pm 20° \leq \alpha \leq \pm 80°$.[63] The results of experiments on the mechanical behaviour of carbon fibre composites under shear, together with data on the influence of various factors on the shear characteristics, have been used to design new types of component with a weight saving of up to 20%.[64,65,67]

The latest technological method of preparing multi-layer PCM relies on the use of a monolithic packet of uniformly oriented reinforcing layers which is itself oriented in different directions. The mechanical properties of multi-layer PCM are largely determined by those of the uniformly oriented reinforcing material. Hence it is relevant to examine theoretical models of the PCM able to predict the strength and the deformation behaviour of the multi-layer material from experimental data on the elasticity and strength of the uniformly oriented material. Both Soviet and foreign publications describe various models of this type which allow for a number of effects accompanying the deformation and fracture of the PCM and ignored in the purely phenomenological approach based on the linear elasticity theory of isotropic solids[68-75].

Experimental studies of the breaking of glass and carbon reinforced PCM have shown that the ultimate failure of these materials is preceded by various impairments (peeling, cracking) which do not exhaust the load bearing the capacity of the composite. It is important to know the types of stress and the stages in loading responsible for the appearance of these initial impairments as well as those responsible for the ultimate mechanical failure.

By combining theoretical models which allow for the layer structure of the material with the maximum stress criteria, and by comparing calculations with experimental results, the principles which determine the breaking of glass reinforced plastics under axial compression, extension, and torsion have been determined for various regions of winding angles[76]. The cause of the disintegration of the binder during the initial deformation and of the final failure of the material under axial extension and torsion has been identified (for different types of glass and carbon fibre reinforced plastics) by using a phenomenological model of the structure of a multi-layer PCM [74] in which a uniformly oriented monolayer is treated as the basic element. By generalising experimental data and various models of the deformation of uniformly oriented composite materials Zinov'ev and Tarakanov[74] have developed a generalised model of the deformation of a uniformly oriented monolayer within a packet of layers which assumes that the matrix of the mechanical characteristics of the uniformly oriented material can have one of eight possible values, depending on the magnitude and sign of the components of the stress tensor and on the sign of the deformation increments. An algorithm for computer calculations was developed from this model. The validity of the results was confirmed by the agreement between theoretical and experimental tensile diagrams[76,77]. It was also shown[69,70] that the torsional fracture of carbon and glass reinforced plastics is induced by compressive stresses along the fibres except in the glass fibre composites with a winding angle $\alpha = \pm 45°$, which break as a result of tensile stresses in a layer at right angles to the fibres. The disjoining stresses in this layer are also responsible for the breaking of glass fibre composites with angles $\alpha = \pm 60°$ and $\pm 75°$ under uniaxial extension. In a glass fibre composite with $\alpha = \pm 45°$ under uniaxial tensile stress the formation of cracks leading to the loss of load bearing capacity is caused by shear stresses. Samples with $\alpha = \pm 45°$ have the highest deformability: their tangential modulus (i.e. the slope of the finite part of the deformation curve) is small on the experimental diagrams and zero on the theoretical. According to this model after the loss of continuity the deformation grows at constant load (assumed to be equal to the limiting load); the proposed algorithm can be used also for loads higher than this limit. In the final stages of deformation we

find a marked increase in the tangential modulus due to the change in the reinforcement angle produced by the deformation, but this does not cause the fibres to break. In glass fibre composites with $\alpha = \pm 60°$ and $\pm 75°$ there is no increase in the tangential modulus, though a high deformability and an increase in deformation at practically constant load are again observed.

Torsional deformation of glass and carbon fibre composites with angles $\alpha = \pm 60°$ and $\pm 75°$ reveals disintegration of the binder as a result of disjoining stresses acting at right angles to the fibres, and of tangential stresses acting along the fibres. The causes of the large-scale failure of the material defined by the criteria given in Refs.74 and 76 for the various winding angles are effectively the same. Because of the special behaviour of $\alpha = \pm 45°$ materials under simple types of load their mechanical behaviour has to be studied with different types of complex loading approximating those experienced by composite materials under field conditions.

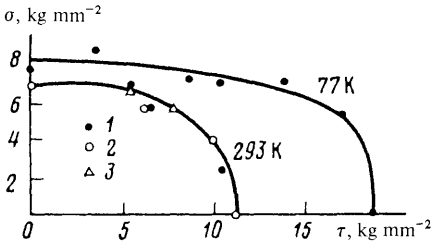


Figure 8. Breaking diagram for an organic fibre plastic at room temperature and at low temperature: *1*) torsion + tension, *2*) proportional deformation, *3*) tension + torsion[78].

Tubular samples of organic and glass fibre composites have been studied[78] for $\alpha = \pm 45°$ and the same epoxy binder under linear deformation conditions under simultaneous axial (tensile) load and torsional moment and with a complex load application curve: tension was used to bring the sample to a prescribed value of σ_i, and torsion was then applied to break the sample at the stress τ_i. The experiment was then repeated in the opposite sequence: a torsional moment was applied to bring the sample to a stress close to τ_i, and then the sample was broken under tension. Breaking diagrams for organic fibre composites loaded in different ways at room temperature and by the complex loading trajectory at low temperature (77 K) are shown in Fig.8. It was found that the experimental values of strength lie on the same breaking diagram for all types of load application. A decrease in temperature produces a marked increase in the strength of organic fibre composites, especially under shear.

IV. PHYSICO-MECHANICAL PHENOMENA IN THE POLYMER FORMATION AND REINFORCEMENT PROCESSES

In this Section we shall review the studies of mechanical phenomena in frontal and in uniform solidification processes, in the heat treatment of polymeric and composite materials, and in their practical applications. Studies of the mechanism of formation of defects and of residual stresses and deformations will also be discussed. The ultimate aim of this group of investigations is to develop favourable technological processes for the large-scale production of thick-walled monolithic components from polymeric or composite materials[79,108,109].

Studies of the chemical kinetics of the solidification of these components have shown[80-86] that the process can be frontal, i.e. spatially non-uniform. Therefore it is important to study the mechanical phenomena accompanying the frontal solidification of articles made from polymers and from reinforced plastics, since defects may be formed or residual stresses may be created.

The problem was solved by postulating[84-90,93] a two-step solidification front, with steps in the liquid and the solid state. This model allows most of the solutions to be obtained in a closed form clearly related to the physical nature of the phenomena and suitable for analysis[93]. Two limiting models were developed for composites: one in which the reinforcing fibres are fully immersed in the liquid binder and a capillary model in which the filler can form a system of capillaries.

By solving various problems in the mechanics of deformation and in hydrodynamics, and by using experimental results, it has been shown that defects can take the form of discontinuities or of residual stresses during frontal solidification[93,94].

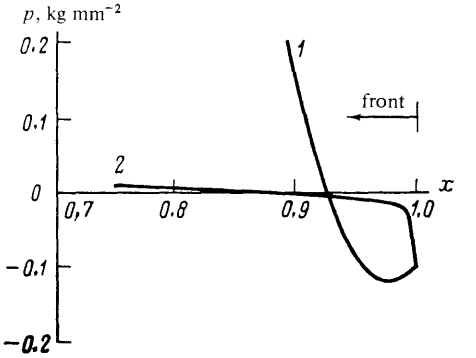


Figure 9. Changes in pressure ahead of the solidification front for a cylinder of reinforced plastic on an elastic mandrel as a function of the position of the front: *1*) stiff mandrel, *2*) stiffness of mandrel reduced by two orders of magnitude; p is the pressure ahead of the front, $x = r/R$ where r is the coordinate of the front and R is the radius of the outer surface of the shell[93].

Fig.9 shows a plot of the changes in pressure ahead of the solidification front in a thick-walled cylindrical shell of reinforced plastic: the front is moving from the outer surface ($x = 1$) towards the mandrel, and the binder is liquid ahead of the front. The fall in pressure ahead of the front to zero or even to "negative" values (i.e. to isotropic expansion stresses) suggests the possibility of slippages or breaks in the continuity of the liquid binder, and the formation of holes and pores (curve *1*); a decrease in the hardness of the mandrel by two orders of magnitude largely avoids the danger of defect formation (curve *2*).

A similar approach can be used to analyse the mechanical phenomena in polymers and in reinforced plastics during a frontal liquid–solid transition, and also in other systems (e.g. liquid–polycrystal, liquid–monocrystal, adhesive–substrate, etc.).

The next stage in the formation of components is heat treatment. This usually consists in cooling the article from the solidification temperature to the storage or application temperature, though additional heat treatment is sometimes applied in order to modify some of the properties of the material. Furthermore, materials and components are often used under conditions of variable temperature, which cause thermal stresses.

The mechanism of formation and development of thermal stresses in polymers was studied with samples consisting of amorphous polymers, both linear [poly(methyl methacrylate)] and with a network structure (epoxy resin)[91-93]. The dependence of the thermal stresses in amorphous polymers on the rate of change of temperature, the quasi-irreversibility of the stresses associated with cyclic changes in temperature, and the increase in stress during isothermal relaxation processes have been demonstrated experimentally and justified theoretically[91-93]. For polymers all these processes are strongly non-linear[93].

Problems of thermal stresses in polymers and reinforced plastics can be solved theoretically by using the full system of equations from classical mechanics which describes the stressed and the strained state, and also the functional relationship between the components of the stress and deformation tensors and time. Phenomenological relationships of the heredity equation type are most widely used. So far little work has been done on the use of physical non-linear coupling equations to describe thermal and residual stresses. A non-linear physical generalisation of the Aleksandrov–Gurevich–Lazurkin equation has been used[93,100] as the coupling equation to describe thermal stresses and relaxation phenomena in polymers by allowing for the first two terms in the spectrum of relaxation times and for the temperature dependence of the elastic and relaxation constants. The validity of this coupling equation in non-isothermal processes has been demonstrated[93] by comparing theoretical results with experimental data.

It has been shown[93-99] that the additional heat treatment applied to amorphous polymers to improve their strength and their relaxation time and to stabilise their properties allows the frozen (residual) bulk and linear deformations produced by the solidification and cooling of the polymer to relax. The influence of frozen linear highly elastic deformations has been used to explain the "well" and "hump" effects on the dilatometric curves of polymers.

Cracks or weaknesses in articles made from reinforced plastics can appear not only during solidification and cooling but also during subsequent storage under static conditions. To account for this phenomenon the thermal stresses and the relaxation phenomena have been studied[93,100,101] in components made from reinforced plastics. A theoretical model of anisotropic materials was developed to explain the relaxation behaviour of the polymer matrix and its interaction with the filler, and a coupling equation for the reinforced plastic under non-isothermal conditions was obtained. This equation is outwardly similar to the Aleksandrov–Gurevich–Lazurkin equation for homogeneous isotropic polymers, but in this case the highly elastic deformation has a different meaning, since it is explicitly temperature-dependent, suggesting interactions between the matrix and the filler[93, 100,101]. Relaxation phenomena in relatively thin articles (for example, made from glass fibre composites) can produce dangerous radial tensile stresses during isothermal storage, thus increasing the probability of crack formation at this stage[100,101]. In thick cylinders relaxation effects cause a substantial decrease in stress during the cooling and storage stages[101].

The influence of residual stresses and deformations on the mechanical behaviour of reinforced plastics and adhesives has been studied with the aid of discrete models of the reinforced plastic[102-107]. This required the development of an approximate theory of the boundary layer, applicable to contact problems in the mechanics of composites. The approach relied essentially on the postulated presence of an intermediate (boundary) layer between the adhesive and the substrate. Its main advantage is the possibility of obtaining "elastic" solutions in a closed form, accurately satisfying all the boundary conditions. Residual stresses created in the model by a layer of polymer during solidification, cooling, swelling, etc. can easily be calculated. This theory can explain the dependence of the measured mean strength of some model reinforced plastics (for example, glues and adhesives) on the geometry and on the experimental conditions (length and area of the joint, thickness of the layer of binder, fibre diameter, stiffness of the adhesive and of the substrate, degree of solidification, shrinkage, measurement temperature, etc.). Methods of calculating correctly the true strength of these composites have been proposed[105-107].

The problem of optimising the cooling conditions of thick-walled articles made of reinforced plastics by the winding method has been examined as a practical application of the theory of thermal stresses. In the formulation of the problem realistic account was taken of the possibilities offered by industrial production plant[110]. The method chosen to avoid crack formation was to use a non-uniform temperature field during the solidification and cooling of the sample[108-110]. This is a problem in non-linear programming with restrictions: the main difficulty in its solution is the non-linearity of the restrictions on the calculated radial stresses at each point in space and time[110].

The effect of various parameters of the problem on the final result has been analysed. A general feature of all the optimisation regimes obtained for articles made from typical reinforced plastics is the more rapid cooling of the outer than of the inner surface. Most of the regimes are monotonic, a very convenient feature in practice. In comparison to the traditional regimes they offer a saving in time of a factor of 4 or better, and they allow the construction of monolithic articles with a wall thickness 5–6 times greater than previously.

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Institute of Chemical Physics of the
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 309-325 (1984) U.D.C. 678.743.22.678.501

Physical and Physicochemical Effects on the Rheological Properties of Polymers during Processing

M.L.Fridman and E.V.Prut

New principles and processes for the treatment of polymers and polymer-based composites are discussed. The controlled effects of physical and mechanical fields on the rheological properties of polymers are analysed as a promising method of developing new component forming techniques. The following topics are discussed: solid-phase extrusion and hydro-extrusion, the cyclic deformation of melts in shear, the interaction of transverse and longitudinal ultrasonic vibrations, and the preparation of ultra-strong films and fibres.
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I. INTRODUCTION

Developments in the chemical technology of plastics during the past 25 years have included some important advances in the application of physicochemical principles in the synthesis of polymers. For example, the method of synthesis of isotactic polypropylene (PP) has suggested possible ways of obtaining other stereoregular polymers; ultra-high molecular weight polymers with a molecular mass (MM) greater than 10^6 have been produced; the polyamide industry can now offer polydodecaneamide (PA-12); new chlorinated thermoplastics have been developed. Lastly, in the Soviet Union the scientific basis of a new production technology for composite materials has been developed: it consists in chemical filling by polymerisation, giving highly filled polymeric composite materials (HPCM) by direct synthesis. These HPCM are called Norplasts (see Refs.1–3 and the review by D'yachkovskii and Novokshonova on p. of this issue).

The conversion of polymers into articles has been carried out by traditional methods (mainly extrusion, injection moulding and pressing). Developments in manufacturing technology have been in scale rather than in kind: larger-diameter extruders have been produced, and the maximum injection volume and speed of rotation of the feed screw in automated thermoplastic production units have been increased. Equipment now available can produce sheet material in widths of 24 m or more, it can mould articles weighing 10 or even 20 kg, it can draw oriented films 2–5 μm thick now and < 1 μm when current developments have been completed, and it can extrude sheets and slabs more than 20 mm thick. However, these achievements have brought the traditional methods close to their ultimate capabilities, and it is evident that a further increase in the size (and hence in power and raw material consumption) of conventional polymer plant cannot be cost-effective.

Further progress in polymer production is likely to result from intensive rather than extensive developments, relying on new methods of forming the wanted articles with much better productivity and product quality and a saving in raw materials and power consumption. The successful realisation of these aims requires the application of the latest advances in the physical chemistry and mechanics of polymers, in the rheology of continuous media, gas-containing media, and dispersed system, and in mathematical modelling and process optimisation methods. We believe that only this approach can offer the substantial improvements in plastics processing techniques which have for many years been the aim of the large teams of specialists working on these important and complex problems in scientific and industrial laboratories.

This paper reviews the scientific basis of some of the new methods of polymer treatment developed under the general direction of N.S.Enikolopov and in many cases from his personal work and ideas.

II. CONTROLLED INTERACTION OF PHYSICAL (MECHANICAL) FIELDS WITH POLYMERS AS A POSSIBLE WAY OF DEVELOPING NEW PROCESSING METHODS

The processing of polymers usually consists in converting the material into a state capable of viscous flow, giving it the required shape, and fixing this shape by cooling (or hardening) of the melt. The production processes include many physical and chemical transformations of the material, such as degradation and cross-linking of polymers, melting, crystallisation, visco-elastic flow, etc. The analysis and control of the process are further complicated by the simultaneous occurrence of most of these changes, with "overlapping" and mutual interaction, so that the individual effects are very difficult to separate and to study.

The properties of polymeric materials and of the articles prepared from them by traditional methods are controlled by two basic and well understood methods: the addition of a plasticiser, and varying the temperature and formation rate regime. Each of these methods has a number of weaknesses. For example, the control of the rheological and technological properties of the basic material by introducing a plasticiser is limited to a relatively small range of polymers by the loss of strength and increase in cost of the finished article: no satisfactory plasticiser has yet been found for the most important of all thermoplastics (polyolefins). Raising the temperature and formation rate can be considered only if the material is stable towards thermal and mechanical degradation, and the danger of loss of quality of the finished article is ever present. The development of new polymers and the ever-growing range of HPCM have created additional problems, arising from the poor thermal stability and very high viscosity of some of the melts, which limit and often preclude the use of standard methods of component production.

Recent work has shown that an effective method of controlling the properties of the polymer during the production process and of optimising the yield of high-quality articles can be based on the controlled action of physical (mechanical) fields on the material, leading to changes in the parameters of the micro- and macro-stresses in the state of the system[4-8]. By controlling the properties of polymers and of composite materials with an appropriate mechanical stress field at the formation stage we can organise the manufacturing processes in an entirely new way and produce articles with a set of properties not accessible by the conventional technology. There are many new methods of forming, but all are based on the same physical principle: the application of controlled mechanical actions on polymers during the formation process. Under these conditions an additional shear stress contributes to the basic flow of the polymer, and the material develops a complicated stress pattern. This deformation scheme can be applied to both solid and liquid substances.

1. Solid-phase Extrusion and Hydro-extrusion

The extrusion of polymers in the solid state by the simultaneous application of high pressure and shear stresses is being intensively studied[9-11] as a method of producing highly oriented materials. Its advantages over alternative methods of producing such materials include the production of articles with a cross-section of unusual shape and a high rigidity and strength from standard industrial polymers. Thus Enikolopov and co-workers[12] have prepared fibres having a strength and stiffness close to the theoretical maximum by extrusion and drawing of PE and PP polymer mixtures. However, because of the wide molecular mass distribution (MMD) of the initial polymers of technical grade a wide range of strength and stiffness parameters was obtained. A more selective specification of initial polymers, with optimum values of the MM, yielded fibres with mechanical properties almost indistinguishable from the theoretical values.

Solid-phase extrusion followed by drawing has been used[13] with a mixture of two high-density polyethylenes: ultra-high molecular weight (MM = 2×10^6) and ordinary (MM = 6.7×10^4). Fibres with a tensile elastic modulus of $E = 222$ GPa were obtained, equivalent to ~ 92% of the E value for the crystalline polyethylene lattice[14].

The structure and properties of the resulting articles are strongly influenced by the basic parameters of the extrusion process (pressure, temperature, etc.). Therefore one of the most essential contributions to this new method is a detailed study and description of the dynamics of the process in the two basic operating regimes: at constant feed rate and at constant pressure. In the first case the extrusion of solid polymers can be likened to the bulk pressing of metals. However, attempts to apply the theory of metal pressing[15,16] to polymer extrusion proved fruitless, because the model does not allow for the special features of plastic flow and orientation strengthening in polymeric materials.

We have recently proposed[9] a model of the extrusion of amorphous–crystalline polymers which assumes a power law for the increase in strength of the material. The following relationship between the extrusion pressure (p_{ext}) and the maximum elongation of the polymer (λ_{max}) was obtained:

$$p_{ext} = \sigma_0 \frac{1 + k \cot \psi}{m + k \cot \psi} (\lambda_{max}^{m+k \cot \psi} - 1) \qquad (1)$$

where σ_0 is the fluidity limit of the polymer before hardening, k is the coefficient of friction at the metal–polymer interface, 2ψ is the feed angle, i.e. the angle at the apex of the conical draw plate, and m is the hardening coefficient of the polymer.

Eqn.(1) satisfactorily describes the experimental results. We note that the extrusion pressure is strongly dependent on the friction at the metal–polymer boundary. Thus very low pressures are needed in the extrusion of Teflon (a polymer with a very small value of k).

Several ways of lowering the boundary friction (and hence the energy consumption) in solid-phase extrusion can be suggested. Firstly, the inner surface of the forming device can be coated with a layer of fluorinated polymer[17]. Secondly, the hydro-extrusion principle is applicable in principle to solid-phase extrusion. The provision of an intermediate hydro-layer lowers the friction between the forming channel and the polymer being processed. However, the practical use of hydro-extrusion is complicated by the tendency of the liquid (especially at high pressures) to diffuse in the surface layer of the polymer where it can cause undesirable changes in properties[11]. Two other approaches to this problem have been suggested in recent years: the application of high-frequency vibrations to the forming device and the provision of a stratified (two-layer) flow of polymer. We know[18,19] that the coefficient of friction can be markedly decreased by applying vibrations of high enough frequency to one of the contacting surfaces of a friction couple. The application of low-amplitude shear vibrations at ultrasonic frequencies (~ 2×10^4 Hz) to the forming device lowers the dry friction almost to zero[19]. This effect offers a substantial improvement in the quality and speed of solid-phase extrusion, giving high-grade products.

The stratified flow of polymers is the basis of the co-extrusion of two-layer and multi-layer sheets, films, filaments, and fibres. The theoretical foundations of co-extrusion were developed in Refs.8 and 20–23. A new way of exploiting two-layer flow[8,24] has been used successfully to accelerate the formation of highly viscous polymer systems (for example, PE with a MM $\geq 10^6$, and HPCM such as Norplasts). Two-layer or pseudo-two-layer flow is created in the forming device, with the layer of low-viscosity component (~ 200–300 μm thick) in contact with the channel wall while the high-viscosity core constitutes the main material. This flow geometry can be achieved by different methods, for example by injecting a low-molecular-weight polymer into the "dead" zones of the input side of the forming device (the "dead zone supply" method), or by adding a low-molecular-weight component to the polymer composition and pressing the low-viscosity component towards the wall of the forming channel (see Fig.1). As a result, the hydrodynamic resistance of the forming device (apparent, or effective viscosity of the system) is greatly reduced, but the properties of the resulting articles are determined by the main material. The formation process in this case can be treated as a special type of hydro-extrusion in which the liquid is replaced by a melt of low-molecular-weight polymer, by a liquid oligomer, or other low-viscosity substances.

An example of pseudo-two-layer flow is given by the production technology of HPCM based on Norplasts. As often reported[25-27], the low-molecular polyethylene into which the Norplast is injected as a filler concentrate is effectively pressed towards the wall of the forming channel, so that the finished articles consist of a "core" of Norplast and an outer "skin" with a low concentration of filler.

The two-layer and pseudo-two-layer flow method could also usefully be applied to solid-phase extrusion to increase the speed of the process and lower its energy consumption. However, experimental tests are needed to identify possible side effects and to characterise the rheologically important changes in flow patterns.

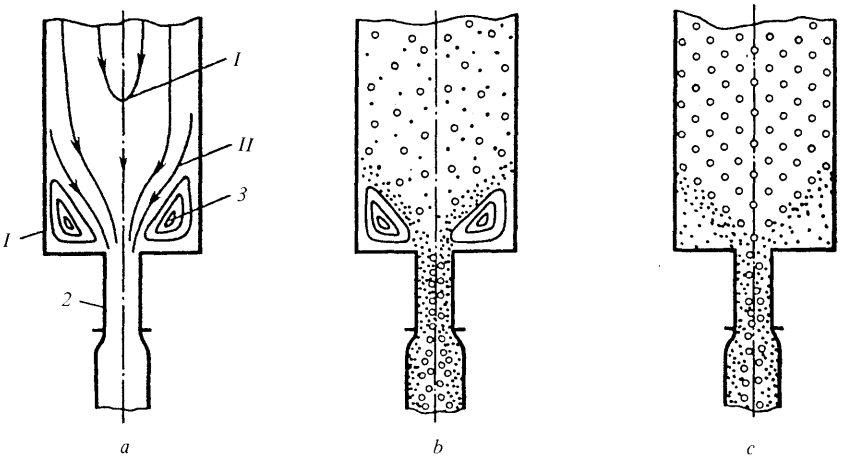


Figure 1. Generation of a two-layer flow in the forming of thermoplastics: (*a*) "dead" zones in the corners of the viscometer cup, (*b*) creation of two-layer flow by introducing a low-viscosity component into the "dead" zone, (*c*) formation of pseudo-two-layer flow by expressing the low-viscosity component from the mixture; *1*) reservoir (or "bomb"), *2*) capillary, *3*) "dead" zone; *I*) line of maximum tensile stress, *II*) line of maximum shear stress[8].

Further developments in solid-phase extrusion should also be aimed at increasing the formation pressure and lowering the formation temperature. These changes should yield materials with improved mechanical properties.

2. Cyclic Shear Deformation of Polymer Melts

Recent work has shown[4-7,28,29] that the complex stress patterns produced in melts by the imposition of additional shear on the basic flow can lower the viscosity of polymeric and dispersed systems. Complex shear can be produced in melts by rotation or by vibration (longitudinal or transverse with respect to the extrusion axis) of the elements of the forming device.

The simplest example of imposed shear is the screw (helical) flow created by forcing the substance through an annular orifice under a constant pressure drop while rotating the cylinders at constant speed (or one of the cylinders, for example the nozzle or the shaft of the extrusion head). An analysis[5,8,30] of helical flow based on the theory of viscous flow[31] has yielded the basic equations for the rheological characteristics of abnormally viscous liquids in terms of the flow conditions and of the geometry of the flow device. The influence of the elasticity of the polymer melts on the extrusion parameters under cyclic shear deformation conditions has been calculated[8,25,30]. The construction and application of extrusion systems with an imposed shear generated by reciprocating rotations of the elements of the forming head (i.e. by low-frequency vibrations of relatively large amplitude) have been discussed in detail[30,31].

Whatever the chosen method of applying the additional shear (rotation of the shaft, reciprocating large-amplitude rotational vibrations, with the moving element located in the pre-inlet chamber or in the forming head itself, and with the vibrations normal to the main flow or coaxial with it) very similar rheological and technological effects are obtained: for a constant drop in pressure in the channels and a constant temperature the viscosity of the polymer and its post-extrusion swelling decrease, and the consumption of liquid and the critical parameters for the onset of unstable flow increase very markedly. For example, in the extrusion of PP reciprocating rotational vibrations of the forming device with an angular amplitude of 22.3° and a frequency of 25 Hz increase the throughput of the extrusion head by a factor of 1.3–1.4,[29] increase the critical flow parameters by 2–5, and lower the swelling coefficient by 1.3–1.5.

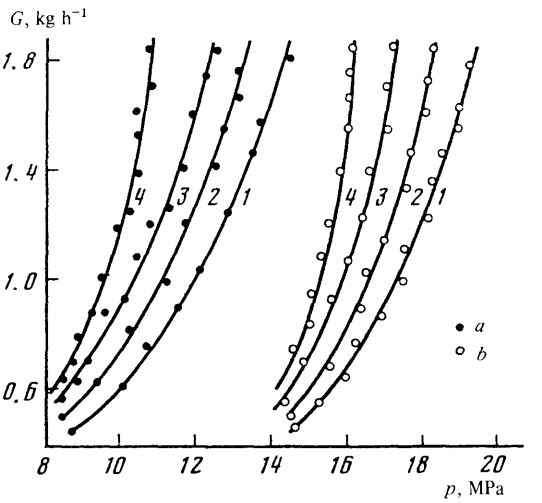


Figure 2. Operating characteristics of the apparatus (plots of the throughput G against the pressure drop in the extrusion head p) for the processing of PP filled with 10 wt.% of chalk (*a*) and 20 wt.% of asbestos (*b*) at 210 °C and different shaft vibration amplitudes: *1*) 0°, *2*) 4.8°, *3*) 11.5°, and *4*) 22.3°[32].

The use of imposed shear is even more effective in high-viscosity systems (for example, filled thermoplastics). Thus in filled polyolefins (30–40 wt.% chalk, carbon black, or asbestos) a 40–80% increase in productivity can be achieved, or if the throughput is kept constant the pressure in the extrusion head can be decreased by at least 20–30% (see Fig.2). Longitudinal vibrations in these melts enhance the orientation effects and produce a slight hardening of the article in the extrusion direction. Reciprocating vibrations of the shaft give a product with isotropic properties, but because of the better homogenisation of the melt the mechanical properties are slightly better (in both directions) than those of the conventionally extruded articles.

We should stress that in spite of the expenditure of power in creating the additional shear by rotation or vibration of the forming elements the overall power consumption of the polymer processing plant is lower (at the highest forming rates) than the power needed to rotate the worm screw in the extrusion through a head (draw plate) with a fixed shaft. Thus forming in the presence of imposed shear may even cause a saving in specific energy consumption[8,29,30]. This effect is most marked in highly filled thermoplastics (for example, asbestos-filled PP[29,32]).

3. Effect of Ultrasonic Shear Vibrations on Polymer Melts

In polymer melts strong vibrational effects can be induced relatively easily by applying high-frequency (ultrasonic, US) vibrations from rod or disk emitters mounted in place of the normal elements of the extrusion head. High-frequency techniques are recommended because the rheological properties of visco-elastic materials are affected by vibrations only above a critical amplitude of the rate of deformation $\varepsilon'_0 = \varepsilon_0\omega$ (where ε_0 is the amplitude of the deformation and ω is the angular frequency), so that at high frequencies we can expect a substantial decrease in effective viscosity[33]. Therefore by using high frequencies we can obtain the desired effect from small-amplitude periodic deformations.

The effect of shear US vibrations has been discussed repeatedly[34–36]. It was shown[37] that the decrease in the largest Newtonian viscosity coefficient of thermoplastic melts produced by US vibrations can be described by the formulae

$$\eta_0 = \eta_{0,0}\exp(-\varepsilon_0/k_1)$$

$$\eta_0 = \eta_{0,0}\exp(-\varepsilon_0'/k_2)$$

Here $\eta_{0,0}$ and η_0 are the largest values of the Newtonian viscosity coefficients in the absence of vibrations (i.e. for $\varepsilon_0 = 0$ and $\varepsilon'_0 = 0$) and in the presence of ultrasound respectively (at a frequency of ~ 20 kHz); k_1 and k_2 are effectiveness coefficients whose value is approximately $k_1 = 1.1 \times 10^{-2}$ and $k_2 = 1100\ s^{-1}$ for a large group of industrial thermoplastics (PVC, PS, PE, and PP).

Using the criterion for the onset of elastic turbulence ($\gamma'_{cr} \cdot \theta_r$) = const (where γ'_{cr} is the critical shear rate and θ_r is the characteristic relaxation time) we can reduce the role of the vibrations to a lowering of the parameter η_0, and hence of θ_r, which allows the parameter γ'_{cr} to rise. Data obtained for polyolefins[8,32,38] confirm that $1/\eta_0$ and γ'_{cr} vary with ε'_0 in the same sense (Fig.3): this conclusion is consistent with the explanation of the effect of vibrations on the rheological properties of melts in terms of a controlled change in the relaxation characteristics, and it also confirms the validity of the assumption that unstable flow is due to a relaxation transition in the polymer.

The use of shear US vibrations in polymer processing technology has been described in detail[8,37,38], and it was pointed out that the new processing method is especially useful in the production of thin sleeve films (up to 10 μm thick) by stabilising the process and giving a product of uniform thickness.

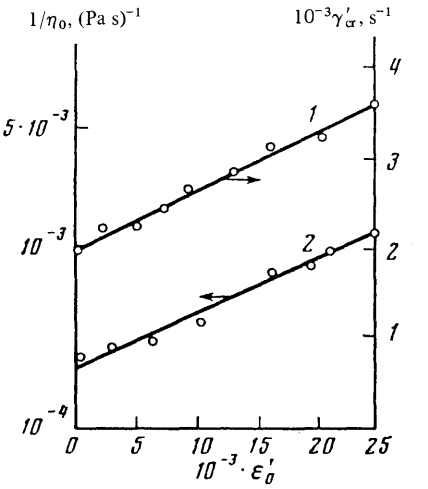


Figure 3. Dependence of the lowest fluidity $1/\eta_0$ and of the critical shear rate γ'_{cr} on the rate of deformation ε'_0 for polyethylene[37].

4. Acoustic Cavitation Phenomena in Fluid Polymers and Compositions Based on Them

The acoustic cavitation (AC) phenomenon is well known in low-molecular liquids, especially in water. However, it has been studied also in solutions of polymers[39–41], and mechanical degradation of the polymer molecules and other secondary effects have been reported for cavitation in low-viscosity solutions. As the viscosity of the liquid increases, we observe a decrease in the mean size and in the rate of growth and collapse of the cavitation bubbles, and the strong secondary effects of cavitation disappear. It was shown both theoretically and experimentally that when the viscosity of the liquid is higher than 1.5–2.0 Pa s the secondary effects of the acoustic cavitation are no longer detectable, i.e. the cavitation is fully suppressed[42,43]. For this reason the acoustic cavitation of polymer melts was not discussed in published papers until recently.

Work carried out between 1978 and 1983 has shown[44–48] that acoustic cavitation can be produced and studied in detail in melts of both model and industrial polymers. It was pointed out that in order to induce cavitation in a melt of a high-molecular polymer the sound pressure level should exceed the bulk strength of the material. Since the strength of a polymer is a minimum in a triaxially stressed state it was reasonable to expect that acoustic cavitation can be excited only by volume US vibrations (as opposed to the shear vibrations considered in the previous Section). For example, in a polymer such as polybutadiene (with a narrow molecular weight distribution and a viscosity coefficient of 10^6 Pa s) the bulk tensile strength is less than 1 MPa,[49] i.e. of the same order as the static bulk strength of ordinary low-viscosity liquids such as water[39], in which AC is relatively easily induced.

By using a special viscometer (with provisions for the application of ultrasound to polymer melts) acoustic cavitation has been detected and its properties have been studied systematically, noting that because of the marked viscoelastic properties of the melts the conditions of formation and the growth and collapse dynamics of the cavitation bubbles are not the same as those in low-molecular low-viscosity liquids.

The AC phenomenon has been observed not only in melts of model polymers (monodispersed polybutadienes) but also in high-pressure and low-pressure PE, PS and PP, and also in HPCM (polyethylene filled with kaolin, chalk, perlite, or glass spheres of average diameter 50 μm[44–48]). Visual observation in ordinary (non-polarised) light and high-speed photography have revealed the formation and growth in an acoustic field of cavitation bubbles which disappear when the source of ultrasound is switched off.

An important experiment was carried out with fluid high-molecular polymers. A small sound pressure detector was embedded in a sample of rubber and connected to an ultrasonic frequency spectrum analyser. It was found that the spectrum of the signal contained, in addition to the fundamental frequency of 17.8 kHz, higher harmonic and subharmonic multiples of this frequency. This phenomenon has been observed many times in ordinary low-viscosity liquids[43], and is typical of AC. It is consistent with the formation in the polymeric liquid of bubbles of resonant size, which suffer strong deformation by the acoustic field and nonlinear changes in the fundamental vibration frequency.

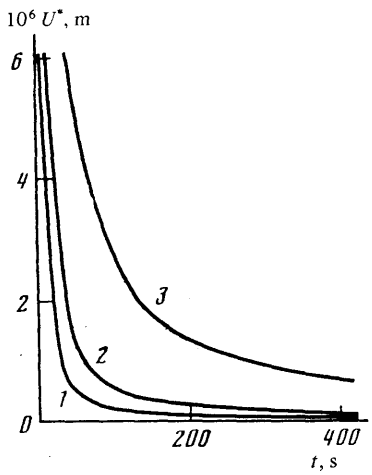


Figure 4. Threshold amplitude of the acoustic vibrations U^* against processing time t of monodispersed polybutadienes of molecular mass MM = 1.6×10^5 (*1*), 3.5×10^5 (*2*), and 5.3×10^5 (*3*)[47].

The following properties and secondary effects of acoustic cavitation in polymer melts have been identified[44–48]. Firstly, the AC is a threshold phenomenon, i.e. each polymer has a characteristic amplitude of acoustic vibrations (U^*) at which cavitation sets in. The parameter U^* depends on time t (see Fig.4), and it is analogous to a long-term strength (durability) function for the polymer[49]. Increasing the MM of the polymer increases its stability towards the formation of AC. The dependence of U^* on t (Fig.4) is described satisfactorily by a power law at low amplitudes of the bulk US vibrations and by an exponential function at relatively large amplitudes:

$$t = A_1 (U^*)^{B_1}$$
$$t = A_2 \exp(B_2 U^*)$$

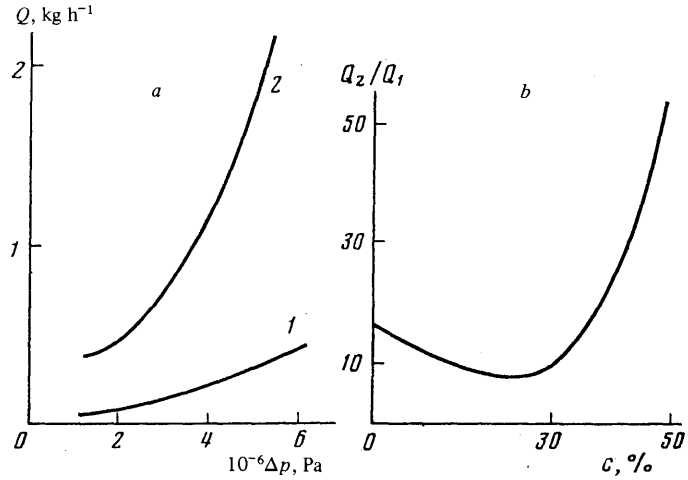


Figure 5. Pressure–flow characteristics of high-density polyethylene (HDPE) melts: (*a*) unfilled HDPE at 264° and acoustic vibration amplitude 0 μm (*1*) and 8 μm (*2*); Q is the flow, Δp is the pressure drop; (*b*) relative flow Q_2/Q_1 (where Q_2 is for the presence and Q_1 for the absence of acoustic vibrations) in HDPE filled with perlite as a function of filler concentration c (temperature 240 °C, amplitude of acoustic vibrations 8 μm)[47].

Secondly, by inducing AC in melts of industrial polymers we can lower the effective viscosity of melts of thermoplastics and HPCM based on them (Fig.5). Depending on the nature of the polymer, on the U^* value, and on other factors, the viscosity can be lowered 5–100-fold, giving a sharp, irreversible increase in the fluidity of the material exposed to the acoustic field. However, this explanation applies only to a part of the increased fluidity (i.e. to the increased throughput). There is a change in the nature (and therefore also in the mechanism) of the flow: the flow collapse phenomenon in the extrusion of the material before exposure to ultrasound is replaced by bubble flow.

Thirdly, in addition to mechanical degradation and changes in the nature of the flow, both of which produce a large decrease in the viscosity of the melt, AC also produces marked changes in the structure of the extruded articles: a decrease in the average characteristic length of the structure elements and a narrower size distribution[48,50], and in the case of filled systems the filler particles become smaller and more uniformly dispersed in the polymer matrix[46,47].

We should stress that the combined effect of these favourable aspects and of the unfavourable mechanical degradation of the polymer matrix caused by the acoustic cavitation is a slight improvement (by 10–20%) in the tensile strength and

in the elongation at break of the extruded articles in comparison to similar articles produced under ordinary conditions[47].

Further studies are needed on the technological aspects of this new phenomenon, which has important consequences in the physics, mechanics, and processing technology of polymers.

5. Production of Ultra-strong, High-modulus, and Ultra-thin Films and Fibres

The preparation of thin and ultra-thin films with the highest possible strength and elasticity from flexible-chain polymers is currently of interest[51]. The main problem is to straighten out the macromolecular chains as far as possible, because this configuration should give an elastic modulus close to the theoretical maximum, though the strength may fall well short of the maximum owing to defects in the structure. Various approaches are possible: multistage film drawing to give an oriented array of chains with the optimum structure, directional crystallisation, setting up a liquid-crystal state in thermoplastics, etc.[51,52].

By developing the concept of orientation by deformation and by applying it in practical systems Enikolopov and coworkers prepared PP films 30–40 μm thick with values of the tensional elastic modulus close to the theoretical maximum[53]: for example, for $\lambda = 28–30$ the mechanical parameters of the films were $\sigma_r = 1.3–1.5$ GPa and $E = 36–43$ GPa.

These results were confirmed by measurements of the velocity of ultrasound (ν_{us}) in polypropylene films prepared with different values of λ.[64] Thus, for $\lambda = 33.7$ and a temperature of 93 K, ν_{us} was 8700 m s^{-1}, a value not previously achieved in oriented flexible-chain polymers. For comparison we note that the ν_{us} value of steel lies between 5 and 6 × 10^3 m s^{-1}, i.e. well below the value for highly oriented polypropylene. The specific elastic modulus E/ρ (where ρ is the density of the polymer) was three times greater for these films than for steel.

These abnormally high mechanical parameters in highly oriented PP can be explained in several ways: the high degree of orientation of the macromolecular chains, the difference in structure between crystalline and amorphous regions (the through chains being more numerous in the latter as well as having a different conformational spectrum), etc.

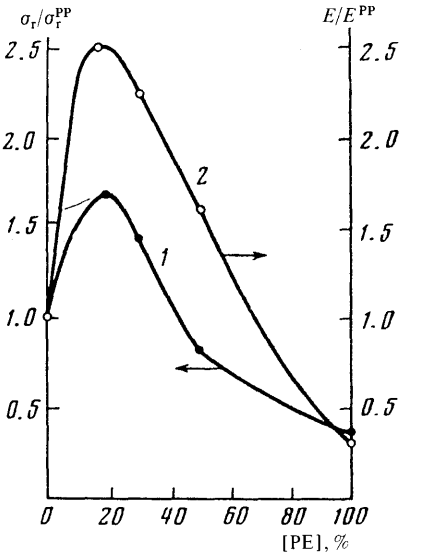


Figure 7. Tensile strength σ_r (*1*) and elastic modulus E (*2*) against composition of PP–HDPE samples for an elongation $\lambda = 15$; temperature of elongation 120–130 °C, σ_r^{PP} and E^{PP} are the tensile strength and the elastic modulus of PP.

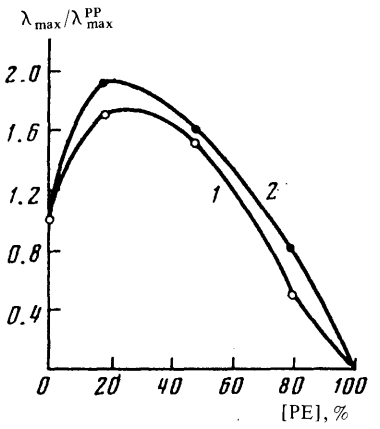


Figure 6. Effect of the composition of PP–HDPE samples on the maximum elongation λ_{max} at different temperatures: *1*) 125, *2*) 145 °C; λ_{max}^{PP} is the maximum elongation of PP.

Polymer–polymer composite materials (PPCM) are another class of potentially useful materials for preparing high-strength, high-modulus thin films. In these films the dependence of the maximum elongation λ_{max} on the composition of the PPCM goes through a maximum (Fig.6). For example, in PP–PE compositions the highest value of λ_{max} is obtained for a PE content of 20–30%. Since the elastic modulus E and to some extent the tensile strength σ_r of the material are monotonic functions of the degree of elongation λ (see, for example, Fig.7) we can expect films with higher values of E and σ_r from PPCM than from single-phase systems.

III. PHYSICOCHEMICAL METHODS OF CONTROLLING THE PREPARATION AND PROPERTIES OF COMPONENTS MADE FROM POLYMERS

Almost any technological process applied to polymer materials is accompanied by a complex set of physical and physicochemical phenomena. This is specially the case when we are concerned not merely with the formation of articles but with developing materials with new and prescribed properties. The approach developed by Enikolopov and his coworkers involves stimulating chemical and physicochemical

changes in the materials by new (non-traditional) methods and studying these changes in polymers and in composite materials under extreme processing conditions.

1. Modification of the Properties of Polymers by High Pressure and Shear Deformation

The processes accompanying plastic flow in polymers under high pressure and shear deformation have been studied extensively in recent years (see the review by Zharov on p.140 of this issue).

One of the most important aspects of this essentially new area in the physical chemistry and mechanics of the solid state is polymer modification. Traditional methods of polymer modification have been reviewed in detail[54,55]. However, the processing of mixtures of polymers and reactive monomers under the combined influence of high pressure and shear deformation offers new possibilities of producing composite materials and articles having specified properties by grafting growing macromolecules onto the polymer matrix. The method can be used, for example, to prepare graft copolymers not available by conventional methods. Thus a conversion of the monomer of ~ 75% has been obtained in studies of the polymerisation kinetics of *N,p*-tolylmaleic imide in a PP matrix, with up to 90% of the resulting polymer grafted to the matrix. As a result of the modification ~ 40% of the composite material was found to be insoluble in boiling tetralin.

It was also shown that forming polymers under these conditions is accompanied by various structural changes (for example, amorphisation and changes in the crystallinity of the lattice[56]), as well as by a large decrease in the molecular weight of the polymer produced by mechano-chemical degradation[57].

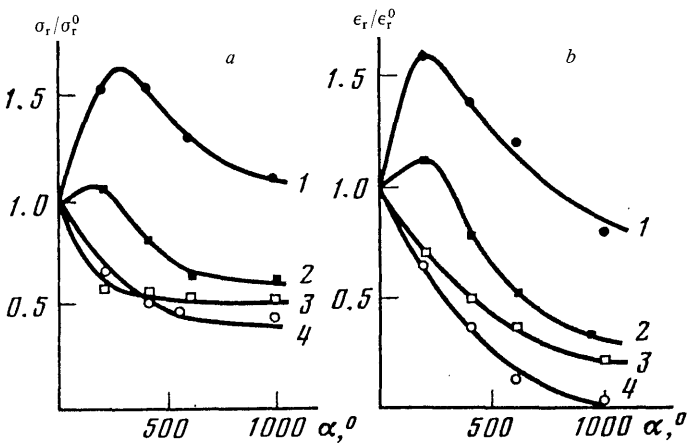


Figure 8. Relative changes in tensile strength (*a*) and in elongation at break (*b*) of samples from PP–SKEP (*1*) and PP–HDPE mixtures (*2*), HDPE (*3*), and PP (*4*), deformed at 10 kbar pressure, as a function of the angle of rotation of the anvil α [58].

The kinetics of these processes are reasonably well described by the relationships usually applied to mechanical degradation processes[41]. We should note, however, that marked differences exist between different polymers: thus in PE mechanical degradation is observed only at pressures above 10 kbar, whereas in PP it sets in at 5 kbar. Lowering the MM of the polymers produces a sharp decrease in fluidity (σ_t), tensile strength (σ_r), and relative elongation at break (ε_r), which converts the fracture from a necking process to a brittle fracture[58].

A very interesting result was obtained in the study of the plastic flow of a mixture of polymers under combined pressure and shear: mixtures of thermodynamically incompatible polymers were found to form a homogeneous system in the amorphous phase under these conditions[59]. As a result the changes in the mechanical properties of the material are not the same as for the homopolymers (Fig.8). We note from curves *1* and *2* of Fig.8 that σ_r and ε_r go through a well defined maximum as a function of the shear deformation in these mixtures for rotation angles of the anvils of 200–300°. The height of the maxima is different in the different polymer systems: for example, in PP–SKEP mixtures the increase in the parameters near the maximum is 60%, but in a PP–PE mixture it is much smaller. We may assume that this marked improvement in the physico-mechanical properties of the mixtures of polymers (as compared with the homo-polymers) is the result of the formation of much smaller and more uniformly distributed heterogeneous phase regions.

The improved understanding of the plastic flow of polymer mixtures under pressure led to the production of high-strength and high-modulus fibres (see above).

To conclude this Section we note that from many points of view (mechanical degradation, decrease in size of the structure elements, amorphisation of the polymers, increased structural uniformity and homogeneity) the effect of combined pressure and shear on polymeric materials is similar to the effect of vibrations, especially the effect of ultrasound in the acoustic cavitation regime. This is consistent with the general principle of using strong physical (mechanical) fields for processing polymers and composite materials.

2. Physico-mechanical and Rheological Properties, and Processing of Polymerisation-filled Plastics (Norplasts)

The principle of polymerisation (or chemical) filling consists in polymerising the appropriate monomer on the surface of a filler (which can be of almost any type: dispersed or filamentary, mineral or organic) after activating its surface with a complex catalyst. This method can be used to produce materials with any desired ratio of polymeric component to filler[1,2].

The wide practical application of these materials (Norplasts) must be preceded by a detailed study of their physico-mechanical, rheological, and technological properties: a series of investigations under the direction of N.S.Enikolopov[25–27,60–63] marks the beginning of this area of research. Because of the multiplicity of the types of material in this new class, of the complexity of their structure, and of their unique properties, extensive and sustained studies are still needed, but some important aspects of the structure and properties of Norplasts have already been established, and the following recommendations for the processing of Norplasts can be formulated.

Whatever the nature of the mineral component, Norplasts are obtained as powders of different particle size. The particles are agglomerates produced by the growing together (or interlinking) of the polymeric coating formed on the

separate particles of the filler. In the Norplasts, therefore, the mineral particles are surrounded by a layer of macromolecules firmly bound to the filler surface by chemical or physical forces. The thickness of this layer is much greater than the thickness of the strengthened surface layers in ordinary filled systems prepared by mechanical mixing of the components followed by granulation on the extruder. The region affected by the presence of the particle of mineral filler is much more extensive in Norplasts than in mixed composites of a similar composition.

At very high filler contents (> 80 wt.%) the Norplasts with a polymeric component of MM $\cong 10^6$ show only elastic deformation. The material develops a tendency to flow only if the amount of "coat" is increased to 40–60% (depending on the MM of the polymer), but a further increase in the amount of polymer (to 80%) does not affect the viscosimetric and extrusion behaviour of Norplasts.

Some interesting effects were observed in studies of the thermal expansion of Norplasts. The temperature dependence of the linear expansion coefficient $\alpha = \Delta l/(l\Delta T)$ (where l is the length of the sample, Δl and ΔT are the increments in length and temperature respectively) includes two maxima: the first at 125–135 °C, corresponding to T_m for the polymeric material, and the second at 180–190 °C. The height of the first peak decreases when the amount of polymer in the Norplast is decreased, and the height of the second peak increases; furthermore, the first peak corresponds to an endo-effect, and the second to an exo-effect. The nature of the second maximum in the $\alpha(T)$ curves is still not fully understood, but we may assume it to be related to the detailed structural features and morphology of the polymeric "coat"[27].

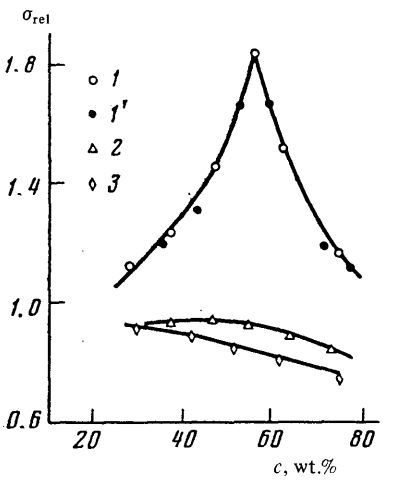


Figure 9. Relative strength ($\sigma_{rel} = \sigma_c/\sigma_m$) of materials as a function of the content of tuff c; compositions with Norplasts containing 12.5 wt.% PE and tuff of average particle size 8 μm (*1*) and 17.2 wt.% PE and tuff of average particle size 80 μm (*1'*); *2*) are model compositions prepared by mixing PE, filler, and ultra-high-molecular-weight PE, 3) are ordinary mechanical mixtures[27].

Structural and morphological studies of the intermediate layers near the filler particles and near the particles of Norplast introduced into a matrix of polyethylene by mechanical mixing have revealed the changes in the number and size of the crystals as a function of distance from the particle surface. In composition containing the pure filler the size of the perturbed region was comparable to the effective radius of the particle, whereas for Norplast it was comparable with the size of the bonded polymer layer. We note that similar effects are observed when the surface of ordinary fillers is treated with dressing compounds. In this sense the Norplast can be described as a filler dressed with a high-molecular-weight polymer of the same nature as the matrix of the main polymer. Since the wear of the equipment is not decreased but is actually made worse by ordinary dressing compounds this method of "dressing" by polymerisation is to be preferred in polymer processing.

The use of Norplasts containing 80–90 wt.% of mineral component as fillers for thermoplastics in the production of HPCM may be technologically preferable to the direct synthesis of the material with the required filler content.

Data obtained so far justify the following conclusions[27]:

a) irrespective of the nature of the mineral filler and of the PE matrix, in Norplast compositions the strength (maximum tensile stress) goes through a maximum as a function of filler content (Fig.9);

b) the strength of the Norplast composites is equal to or greater than the strength of the basic PE over practically the whole range of filler concentration in the material (30–70 wt.%);

c) the relative elongation at break of a HPCM containing Norplasts is close to that of the basic polymer at the fluidity limit, whereas it is lower in ordinary mixed compositions;

d) for a fixed content of the mineral component in composites the strength characteristics increase with the amount of polymeric component (i.e. with the thickness of the "coat") in the Norplasts;

e) the specific shock viscosity of materials filled with Norplasts is higher than for ordinary mixtures of the same composition;

f) the wear of the parts of the processing plant is much lower for HPCM containing Norplasts than for mechanical mixtures with conventional fillers.

A systematic study of the rheological (viscous, and viscoelastic) properties of these new materials[25,27,60–62] has shown that for a fixed shear stress (τ) the relative viscosity of the compositions $\eta_{rel} = \eta_c/\eta_m$ (where η_c and η_m refer to the composition and the matrix polymer respectively) is uniquely determined by the content by volume of Norplast in the mixture, and that for a fixed filler content the viscosity of the system increases with the amount of polymeric component in the Norplast used as a filler concentrate.

We note that undesirable "blocking" effects (with formation of a "stopper" of filler at the mouth of the forming channel) do not take place during the extrusion of Norplasts, though they are common in the pressing of ordinary HPCM mixtures.

The addition of fillers to linear polymers produces flow collapse (Fig.10) even if the effect is absent in the base material[26,27,60]. Increasing the concentration of filler or decreasing the length of the channel and the volume of material in front of the channel tends to convert the pressure–flow curves from characteristic hysteresis loop curves into flow curves with a break. The effective value of the stress τ_{cr} or of the flow Q_{cr} corresponding to the onset of collapse decreases as the concentration of filler in the system increases, but the effect is slight and for practical calculations the parameter τ_{cr} can be assumed to have the constant value 2.5×10^5 Pa.

Lastly, in all HPCM (whatever the nature of the matrix and of the filler) a sharp increase in the pressure drop at the inlet is observed over a well defined range of temperature and strain rate (the Bagley correction). In the case of the Norplasts the increased loss of inlet pressure for a given concentration of mineral filler sets in at lower extrusion rates, as shown in Fig.11. Typically, the sudden step in the loss of inlet pressure occurs at τ values corresponding to the flow collapse in linear PE.

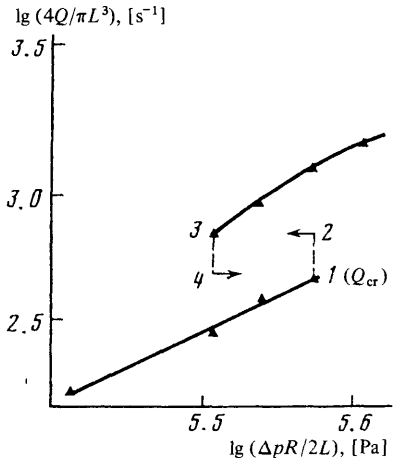


Figure 10. Flow curve for a PE composition containing 30 wt.% of perlite introduced as a Norplast; capillary size 1 mm × 30 mm, temperature 200 K. Point *1* (Q_{cr}) corresponds to the onset of pressure self-oscillations of amplitude equal to the distance between lines *1–2* and *3–4*; the arrows denote the onset of flow collapse (Q is the flow, Δp is the pressure drop, R is the channel radius, and L is the channel length)[27].

The addition of Norplasts to compositions lowers the swelling of the extruded product very considerably, thus assisting the production of shaped articles with improved dimensional tolerances.

Equations and procedures for predicting the viscosity properties of composites filled with Norplasts have been proposed[25–27,61].

Thus recent work has demonstrated the value of Norplasts as components of HPCM offering a prescribed set of properties. This allows us not only to improve the strength characteristics but also to decrease the wear on the extrusion devices (as compared with similar compositions prepared from mechanical mixtures by the traditional technology). The processing of these materials should be carried out in equipment with forced feed (single-screw extruders with a channelled sleeve in the load region, or double-screw extruders) with an attachment for degassing the melt. As in the processing of mixed compositions, the extrusion machinery must have a high-power drive as compared to the extruders for pure polymers.

Further work on these materials should be aimed at the structural and morphological properties of composites containing Norplasts and at determining their long-term stability. We can hope that new materials with a high long-term stability (durability) will emerge from current work on polymerisation filling.

There is little doubt that important advances in the industrial treatment of plastics can be expected from the more general application of mechanical and acoustic fields to polymers in the viscous liquid or the solid state.

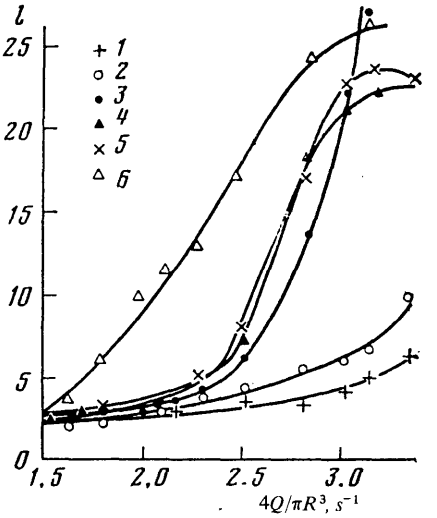


Figure 11. Dependence of the inlet effect (length of the inlet region l) on the normalised volume flow for PE–Norplast (perlite) compositions with different concentrations of filler: *1*) 0, *2*) 10, *3*) 20, *4*) 25, *5*) 30, *6*) 40 wt.%; temperature 180 °C[27].

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"Plastik" Scientific Industrial Department,
Moscow Institute of Chemical Physics of the
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 326-346 (1984) U.D.C. 536.46+541.124+678.01

The Combustion of Polymers and the Mechanism of Action of Fire-proofing Agents

N.A.Khalturinskii, T.V.Popova, and A.A.Berlin

The sequence of stages involved in the combustion of polymers—ignition, flame propagation, and burn-out—has been examined. The limits of existence of the flame and the role of radiation in combustion processes have been discussed. The influence of halogen- and phosphorus-containing fire-proofing agents on the combustion processes has been analysed. The promising possibilities provided by micro-encapsulated fire-proofing agents have been demonstrated.
The bibliography contains 130 references.

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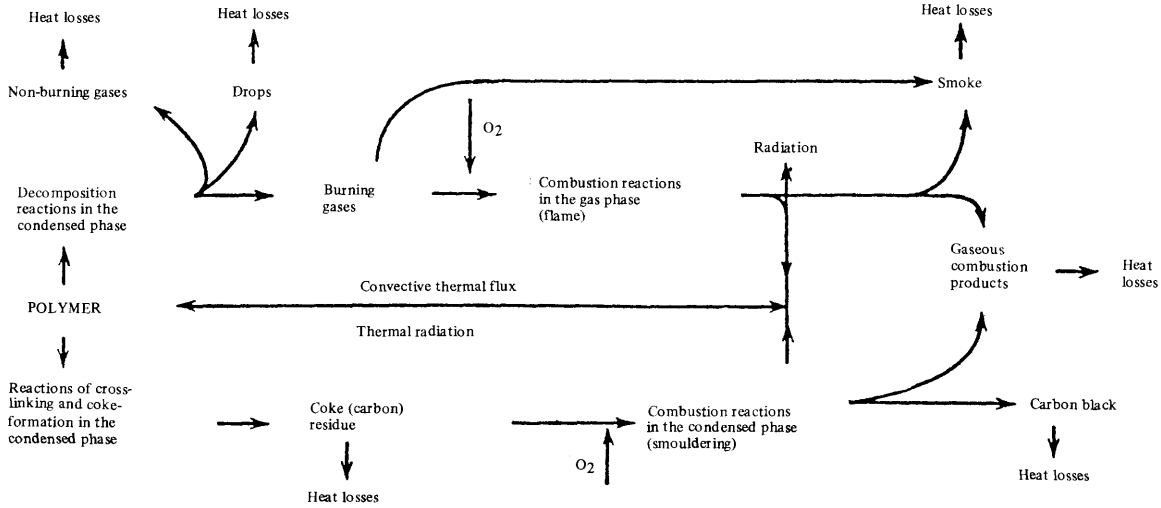
I. INTRODUCTION

Polymers are finding increasing application in various branches of the national economy, but in a number of fields the increase in their use is being held back because of the increased fire hazard associated with materials based on them. This applies particularly to polymers in building, transport, the electrotechnical industry, and other fields. Thus the problem of decreasing the combustibility of polymers and the development of non-combustible materials based on them is one of the most important tasks in polymer chemistry.

Most work aimed at lowering the combustibility of polymeric materials has been and is being carried out on the basis of an empirical search for fire-proofing additives. In recent years, under the direction and with the active participation of Academician N.S.Enikolopov, fundamental studies have begun and are being successfully continued in the Soviet Union in the field of the combustion of polymers and the mechanism of the action of inhibitors. The results of these studies make it possible to formulate the principal ways to reduce the combustibility of polymers and to create non-combustible materials based on them.

The sequence of phenomena in the combustion of polymers can be represented by a scheme which shows that the combustion of polymers is a complex multi-stage process which maintains itself and is controlled by mass and heat transfer[1-4]. The products of the transformation and gasification of polymers are various hydrocarbons[1], so that the diffusion combustion of polymers is largely analogous to the combustion of gaseous and liquid hydrocarbons.

The combustion of polymers is a process that develops with time. Five basic stages in the development of this process can be distinguished: ignition, flame propagation, combustion itself, smoke formation, and collapse of the flame[5]. It is possible to distinguish provisionally five spatial zones in the combustion of polymers: a polymer heating zone, a zone



of chemical transformations in the condensed phase, a zone under the flame, the flame itself, and a zone of reaction products and oxidant[1].

From the above qualitative scheme for the combustion of polymers, it is possible to reach preliminary conclusions about the paths leading to a lowering of the combustibility of polymeric materials. These are primarily an increase in the heat of gasification L, a decrease in the supply of heat to the polymer by increasing the heat losses or by decreasing the heat of combustion Q or by lowering the temperature of the flame by diluting it with non-combustible thermal degradation products[1,3]. It is usually assumed that the formation of a carbonised residue insulates the polymer from heating by the flame[4]. Smoke formation indicates incomplete combustion of the fuel and a decrease in the heat of combustion, and also makes it possible to reach qualitative conclusions about the degree of combustibility of polymers[6,7]. The chemistry of the processes taking place in a polymer gas flame is extremely complex, and has still been insufficiently studied. This question has been dealt with in a number of recent publications[1,8].

The mechanism of the influence of inhibitors on the various stages of the combustion of polymers has not yet been finally resolved. Generally speaking, only qualitative schemes for the action of fire-proofing agents have been published. In this connection, the study of the regular features of the combustion process, and the influence of fire-proofing agents and gas-phase inhibitors on this process and on reactions in diffusion flames in general, is of considerable scientific and practical interest. The aim of the present review is to examine work published up to the present on this problem, and to summarise the results obtained.

II. PROCESSES INVOLVED IN THE IGNITION OF POLYMERIC MATERIALS

The development of theories of flame production and ignition began with the thermal theory of explosion developed by Frank-Kamenetskii[9]. Because of the variety of polymeric materials and the conditions of their application, it is possible in practice to have ignition processes of different types, which do not fit into the framework of a single sufficiently simple theory. The ignition process is often determined by an induction period, during which the surface layer of a substance is heated to a temperature determined by the conditions of stationary combustion, with simultaneous initiation of the combustion of the gaseous products of the thermal decomposition of the polymers.

Since up to 80% of fires arise from low-calorie sources[1], it is appropriate to pay particular attention to the ignition of polymers by these sources. At the present time there are many theories of ignition to describe systems reacting in the condensed phase[10], but these theories cannot explain the observed practical dependence of the ignition process on the conditions of the surrounding gaseous medium and do not take account of the probability of endothermic reactions involving degradation of the polymer in the condensed phase. The models of ignition in the gas phase published up to the present are one-dimensional models in which the source of the oxidant is the surrounding gaseous medium, and the source of the fuel is the products of the gasification of the solid polymer.

The ignition process is initiated by the transfer to the polymer of the heat from the source, which may be an electric discharge, a heated body, a burner flame, etc. In contrast to theories of the ignition of a condensed fuel, in the case of the ignition of polymers it is necessary to bear in mind that: 1) when a thermal flux acts on a polymer, its gasification begins at a rate which depends on the thermal flux power[14]; 2) the temperature at the polymer surface (T_s) is determined by the thermal decomposition conditions[11]; 3) the products of the thermal decomposition of the polymer mix with the oxidant, forming a "previously mixed" mixture; 4) when the gaseous phase reaches critical conditions, ignition of the mixture takes place[12], that is exothermic oxidation reactions are initiated; 5) the relaxation time of the processes taking place in the gas phase τ'' is extremely short compared with τ', that is the relaxation time (the time of the change in the heat distribution in the condensed phase): $\tau'/\tau'' \cong 10^4$;[13] 6) the time of ignition delay, that is the attainment of conditions in which ignition has taken place in the gas phase and the polymer specimen is able to burn in the absence of the source, is determined by the time taken to create the necessary heated layer in the condensed phase[14].

When an ignition source acts on a polymer and the resulting mixture of oxidant and thermal decomposition products, the initiation of the wave of the chemical reaction in the gas phase takes place in accordance with the theory of the ignition of a hot mixture by heated surfaces[12] in the case where the removal of heat from the heated surface (q_*) reaches a critical value, defined by the relationship

$$q_*^2 = 2\lambda'' \frac{RT_s^2}{E} Qk_s e^{-E/RT_s}$$

where λ'' is the thermal conductivity of the gas phase, T_s the temperature of the heated surface, E the effective activation energy of the reactions, Q the heat of the reaction in the gas phase, and k_s the pre-exponential factor in the expression for the rate constant of the chemical reaction. The right-hand part of the expression for the thermal flux contains the kinetic characteristics of the chemical reaction taking place in the gas phase; the quantity q_* is determined by the conditions of heat exchange between the hot wall and the surrounding gas. As a rule, when polymers are ignited by heated solids, there is produced (as a result of natural convection) a stream of gas which flows over the heated surface. The field of flow of the gas stream is determined by the rate of flow and the shape and characteristic dimensions of the solid.

Table 1. Values of the parameters of the ignition process for a number of polymers*.

Polymer	T_i, °C	OI	T_{fp}, °C	T_{sfp}, °C
Polyformaldehyde	975	15.1	—	—
Polystyrene	1002	18.1	296	491
Polymethyl methacrylate	1050	17.5	280—300	450—462
Polyethylene	1055	17.4	341	349
Polyamide	1075	25	421	424
Polycarbonate	1176	28	—	—
Polyvinyl chloride	1260	45	391	454

*T_i values from Ref. 13; OI, T_{fp}, and T_{sfp} from Ref. 16.

Table 1 gives experimental data on the temperature of the surface of a heated solid $T_s = T_i$, where T_i is the temperature at which ignition of the degradation products of the

polymers takes place under conditions of identical heat exchange. For comparison, Table 1 gives the values of the oxygen index (OI), the temperature of flame production T_{fp}, and the temperature of spontaneous flame production T_{sfp}. The limiting characteristics, that is the OI values characterising the combustion process, change in the same sense as T_i, which determines the kinetics of the chemical reactions in the gas phase. The values of T_{fp} and T_{sfp} are apparently integral characteristics which include the thermophysical characteristics of the material, the geometric dimensions of the specimen and the compartment, the flow rate, etc., so that there is no direct correlation between these values and T_i.

Since in some branches of industry polymeric materials are used at increased concentrations of oxygen in the atmosphere, it is important to discuss the dependence of the ignition temperature on the oxygen concentration. The data in Fig. 1 [13,14] show that in mixtures enriched in fuel, the ignition temperature decreases with increase in the oxygen concentration; at an oxygen concentration in the mixture greater than the stoichiometric concentration, T_i is independent of the oxygen concentration ($[O_2]$).

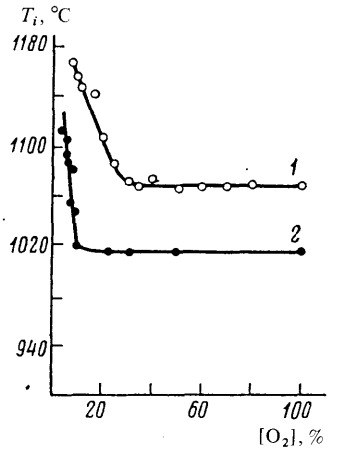


Figure 1. Dependence of the ignition temperature of the polymer on the oxygen concentration: *1*) polymethyl methacrylate[13,14]; *2*) polyoxymethylene[13].

Another characteristic determining the ignition of the material is τ_i, the time taken to create a heated layer, or the ignition delay time. With the assumption that the condensed phase is chemically inert[15], the necessary condition for ignition was found, namely that at the temperature of the polymer surface T_s the temperature gradient should not be greater than that given by the expression:

$$\frac{dT}{dx} = \frac{\rho' C_p''}{\lambda'} \frac{2RT_s^2}{E} \cdot \frac{u'}{e}$$

The ignition delay time[15] is given by

$$\tau_i = \frac{(T_s - T_0)\, EC_p'}{2RT_f^2 C_p''} \cdot \frac{\varkappa' e^2}{(u')^2}$$

where C_p'' and C_p' are the heat capacities of the gas and condensed phases respectively; ρ', λ', and $\varkappa'$ the density, thermal conductivity, and temperature conductivity of the condensed phase respectively; T_f the flame temperature, and T_0 the temperature of the polymer.

The heat required to create the heated layer is calculated using the equation

$$q_i = \frac{(T_s - T_0)^2 C_p'}{2RT_f^2 C_p''} \cdot \frac{\rho' e}{u'}$$

The regular features observed[15] cannot be transferred completely to the case of the combustion of a polymer, since, firstly, no account was taken of the endothermic reaction of thermal decomposition in the condensed phase and, secondly, during ignition the ignition source (for example a heated body) is present in the flame zone.

The conditions of existence of a stationary combustion front have been found[17] from an examination of the conditions of preservation of the mass fluxes of the oxidant and the fuel and the preservation of the thermal flux. The model examined includes a diffusion flame in the gas phase, the endothermic reactions of thermal decomposition in the condensed phase, and the production of the heated layer. Using these data[17], the present authors found that the ignition delay time is proportional to the temperature conductivity of the polymer $\tau_i \cong \text{const}\, \varkappa_1$, as in the expression obtained in Ref. 15. In addition, the data[17] were used to obtain the dependence of the ignition delay time on the oxygen concentration in the surrounding medium:

$$\ln \tau_i \simeq -2 \ln [O_2] + \text{const}$$

These conclusions are confirmed by experimental data on the dependence of the ignition delay time on the thermophysical characteristics of the polymers and the concentration of oxidant in the stream[13,18,19].

III. REGULAR FEATURES OF THE COMBUSTION OF POLYMERS

After stationary combustion conditions have been established close to the ignition source, depending on the conditions of the surrounding medium (the oxygen concentration, pressure, temperature, the velocity of the incoming flux), the thermophysical and thermochemical properties, the geometry of the specimen, etc., two cases may be realised. The flame either is localised or extends over the surface of the polymeric material, leading to an increase in the combustion region and the complete covering of the burning material by the flame. Since the consequences of a fire depend on the size of the combustion region, considerable attention has been paid in the literature to the separate topic of flame propagation[20-33].

Since an exact solution of the two-dimensional problem of flame propagation is not possible, a number of approximate models exist. The problem of the propagation of a flame over the surface of a polymeric material is usually divided into two cases. The first case corresponds to the propagation of the flame over the surface of a specimen of the polymeric material, the thickness of which is much greater than the thickness of the heated layer. These materials are usually classified as thermally thick fuels. The second case is when the thickness of the polymer specimen is comparable with the thickness of the heated layer; these are thermally thin materials. In addition, the exchange of heat between the flame and the polymer surface depends markedly on the direction on the rate of flow of oxidant relative to the rate of flame propagation[20,21].

Thus in De Ris' model[28], flame propagation over thermally thin and thermally thick fuels is examined with the assumption that for thermally thin fuels, heat transfer from the flame through the gas phase predominates, and that for thermally thick fuels, heat transfer takes place through the condensed and gas phases without allowance for the radiation from the flame. For thermally thin layers, the rate of propagation of the flame reaction is inversely proportional to the thickness of the layer of fuel

$$v = \frac{\sqrt{2\lambda'}}{\rho' C_p' \delta} \cdot \frac{T_f - T_s}{T_s - T_0}$$

where 2δ is the thickness of the layer of fuel. For thermally thick specimens, the following expression was obtained:

$$v = \frac{\rho'' C_p'' \lambda'' v_a}{\rho' C_p' \lambda'} \left(\frac{T_f - T_s}{T_s - T_0} \right)^2$$

where v_a is a parameter defining the rate of the incoming flow of oxidant.

Subsequently, models of flame propagation were proposed[29,32], in which the solutions of the equations of heat and mass cotransfer for the gas and condensed phases are examined, and subsequently combined; the dependence of the rate of flame propagation on the parameters of the medium and the characteristics of the polymer obtained in this way are given below. For thermally thin polymers:

$$v = \frac{\lambda' Q_c [O_2] f(p, [O_2])}{L \rho' C_p' (T_s - T_0)}$$

For thermally thick polymers:

$$v = \frac{[\lambda'' Q_c [O_2] f(p, [O_2])]^2}{\lambda' \rho' C_p' C_p''^2 (T_s - T_0)^2}$$

Here, Q_C is the heat of combustion of the polymer, p the pressure, and $[O_2]$ the oxygen concentration in the stream. These empirical relationships were confirmed experimentally[33]; the relationships obtained do not make it possible to obtain a physical picture of the process, however.

Solution of the equations of the thermal balance in the edge of a propagating flame (with the assumption that the transfer of heat from the flame to the polymer takes place as a result of convective heat exchange and radiation) [30,34] gave the following expressions for the rate of propagation of the flame over thermally thin fuels[34]:

$$v = \frac{1}{C_p' \rho'} \left(\frac{\lambda'}{\beta \delta} \right)^{1/2} \left[\frac{2(T_f - T_s) + Q_r}{T_s - T_0} \right]^{1/2}$$

and thermally thick fuels:

$$v = \frac{\alpha (T_f - T_s) + Q_r}{\beta \rho' [L + C_p' (T_s - T_0)]}$$

where α is the heat exchange coefficient, L the heat of gasification of the polymer, Q_r the thermal flux of radiation from the plane, and β a coefficient relating the rate of propagation of the flame to the rate of linear thermal decomposition in the nose of the flame. The expressions obtained contain in explicit form the dependence of the rate of propagation of the flame on the parameters of the external medium and the characteristics of the polymer. Although this model is approximate, it effectively describes the published experimental data.

To characterise the combustion of polymers under the conditions of the stationary (relative to the surface) diffusion edge of a flame (for example the combustion of polymers in a counter-current of gaseous oxidant, when a planar flame is created), Spalding introduced the parameter B (the Spalding number), which characterises the intensity of heat and mass exchange in the system and arises in the solution of the equations of heat and mass transfer at the phase boundary[1]. In the case of convective and molecular heat transfer, the parameter B is defined by the equation

$$B = \left\{ \frac{[O_2]}{r} \cdot Q_c - C_p'' (T_s - T_0) \right\} / L$$

where r is the stoichiometric coefficient of the oxidation reaction.

The rate of diffusion combustion ($\dot{m}$) in this case is given by the expression

$$\dot{m} \simeq \ln(1 + B)$$

The parameter B is an important characteristic for estimating the degree of combustibility of materials, and methods have been developed for calculating it for various materials by the treatment of experimental data on combustion for the configuration of a planar flame with sweeping by the oxidant from above downwards in a counter-current flame[35-38]. The values of the parameter B have been determined[37] for various polymers with sweeping of the flame by a stream of oxidant, and account has been taken of the contributions of various mechanisms of heat transfer to the quantity B for combustion in air and in oxygen (see Table 2).

Table 2. Values of the transfer parameter B for various polymers[37].

Polymer	Parameter B	
	in air	in oxygen
Polymethyl methacrylate	1.38	13.6
Nylon 6-6	1.2	14.0
Polyvinyl chloride	0.9	7.0
Polypropylene	0.67	11.6
Polystyrene	0.6	9.4
Low-density polyethylene	0.58	10.3
High-density polyethylene	0.55	9.7
Untrated cardboard	0.51	4.5
Cardboard containing 16% inhibitor	0.41	3.8
Cardboard containing 25% inhibitor	0.17	2.2
Maple	0.16	2.1

IV. LIMITS OF EXISTENCE OF A DIFFUSION FLAME FOR POLYMERS

A number of studies have shown that the products of the transformation of polymers and gaseous and liquid hydrocarbons in the zone under the flame are practically the same[1,40-44]. Collapse of the polymer flame takes place in the gas phase for the same reasons as in gaseous diffusion flames.

The foundation of the theory of diffusion combustion was laid by Burke and Schumann[12], who were the first to examine the problem of the combustion of coaxial parallel gaseous streams of fuel and oxidant. It is suggested that the chemical reaction in the flame takes place infinitely rapidly (much more rapidly than diffusion), and the form of the flame is determined by the rate of diffusion. In this model, the flame represents an infinitely thin surface with the oxidant on one side and the fuel on the other; the fluxes of oxidant and fuel reaching the flame are in the stoichiometric ratio. Hottel and Hawthorne[45] were the first to confirm experimentally the concept of the flame as a combustion surface with the fuel on one side and the oxidant on the

other. The calculated temperature of the flame in the reaction zone coincides with the adiabatic temperature of the previously mixed mixture of fuel and oxidant.

The conclusion that limits of a diffusion flame exist was first reached by Zel'dovich[46], who solved the one-dimensional problem of the combustion of complex streams of fuel and oxidant moving in opposite directions. With increase in the intensity of the fluxes of fuel and oxidant reaching the flame zone, the latter becomes broader (assuming a single-stage chemical reaction with a finite rate) and the temperature of the flame zone decreases to the minimum possible value (T_f^*):

$$T_f^* = T_f - 3RT_f/E$$

Collapse of the diffusion flame takes place because the chemical reaction, whose rate is exponentially dependent on temperature, is not fast enough to process the substance (fuel, oxidant) reaching the flame and cooling it, and this leads to further cooling and extinction of the flame. Collapse of a diffusion flame may take place similarly with a constant flux of oxidant and decrease in the concentration of oxygen in it. In practice, a diffusion flame is colder than predicted by theory[12], since an important role in the thermal balance is played by heat losses as a result of radiation into the surrounding medium, not usually taken into account in the theory.

In the analysis of the limiting conditions of a diffusion flame, it is convenient to use the parameter: $\mathrm{Dam} = \tau_d/\tau_c$, where Dam is the Damkohler number, τ_d the characteristic diffusion (convection) time, and τ_c the characteristic time of the chemical reaction[12].

A simplified form of the expression for the Damkohler number for a diffusion flame has been given[8]:

$$\mathrm{Dam} = \tau_d \cdot [\mathrm{F}] \cdot [\mathrm{O_2}] \cdot \frac{B}{[\mathrm{O_2}]} \cdot e^{-E/RT}$$

where τ_d has the same order of magnitude as the ratio l/w in the case of forced convection (l is the characteristic dimension, and w the rate of sweeping) or l^2/D in the case of diffusion; D the coefficient of mutual diffusion of the fuel and the oxidant; and [F] the concentration of the fuel. Collapse of the flame takes place at $\mathrm{Dam} = \mathrm{Dam}_{cr}$.

This expression, in particular, leads to a number of possible methods for inhibiting combustion by collapse of the flame[8]: 1) isolation of the fuel and a consequent decrease in its concentration in the flame; 2) decrease in the concentration of oxidant; 3) cooling of the condensed fuel and oxidant; 4) inhibition of homogeneous and heterogeneous reactions; and 5) increase in the rate of sweeping of the flame by the oxidant.

All these methods in the final analysis are directed towards a decrease in the flame temperature; instead of the condition for collapse of the flame $\mathrm{Dam} = \mathrm{Dam}_{cr}$, where Dam_{cr} is the value of the Damkohler number at the combustion limit, it is possible to consider the condition $T_f = (T_f)_{cr}$, where $(T_f)_{cr}$ is the flame temperature at the combustion limit[8]. On the basis of this equation, in the case where the value of $(T_f)_{cr}$ and the other necessary parameters of the system are known, it is possible to calculate the limiting conditions for the flame from the thermal balance equations[8].

The theory of the limits of a diffusion flame was subsequently developed[41-44] for polymers undergoing degradation and gasification without a residue, for the configuration of a planar diffusion flame. It was shown[47-51] that there is a relationship between the limiting conditions of combustion of polymeric materials and heat losses of different kinds. Equations were obtained, describing the influence on the critical conditions of convective and conductive heat losses and heat losses due to radiation, and the phenomenon of "break-through" of the fuel and oxidant through the flame zone as a result of incomplete combustion was calculated theoretically.

Another approach to the determination of the limiting conditions of the combustion of polymers, based on the thermal balance equation, is possible. Thus a model of the candle-like combustion of polymers has been examined[52] and made the basis of an experimental method for determining the limiting minimum oxygen concentration supporting candle-like combustion under conditions of natural convection.

V. HEAT TRANSFER BY RADIATION AND ITS INFLUENCE ON THE COMBUSTION OF POLYMERS

The role of radiation in diffusion combustion was first pointed out by Blinov and Khudyakov[53], who studied the dependence of the rate of combustion of the fuel under conditions of natural convection in air on the characteristic dimension of the combustion region. Beginning from a diameter of the combustion region of ~20 cm, the mechanism of the transfer of heat from the flame to the fuel changes from convective to radiative heat transfer[8]. Radiation from the flame on the one hand leads to increase in the supply of heat to the polymer and to an increase in the rate of combustion of the polymer and the rate of flame propagation, and on the other hand to a decrease in the flame temperature as a result of heat losses to the surrounding medium, a decrease in the width of the flame zone, and a decrease in the conductive and convective heat transfer.

Table 3. Various parameters* of the combustion of polymers in air under conditions of natural convection[55].

Polymer	T_f, K	$Q_{r.f}$, W cm^{-2}	Q_{con}, W cm^{-2}	$Q_{r.s}$, W cm^{-2}	$10^4 m$, g cm^{-2}s^{-1}	γ
Polyoxymethylene	1400	5	17.5	6.7	6.5	1.0
Polymethyl methacrylate	1400	20.1	7.62	10.7	10.5	0.85
Polyacrylonitrile	1350	28.7	6.84	18.2	8.5	0.87
Polystyrene	1190	37.2	2.9	14.6	14.5	0.57

Notation: $Q_{r.f}$ is the radiation heat flux to the polymer, Q_{con} is the convective heat flux from the flame to the polymer, $Q_{r.s}$ is the thermal radiation from the polymer surface, and γ is the degree of completeness of combustion.

There have been a number of studies of the influence of radiation on the combustion of polymers. Thus the influence of radiation on the combustion of polymethyl methacrylate in air has been analysed theoretically for the case of a one-dimensional flame of small dimensions[54]. An important role is played by radiation from the polymer surface, which is responsible for heat losses and heating of the flame. Completeness of combustion has practically no influence on the rate of burn-out of the polymer, since with decrease in the completeness of combustion there is a simultaneous decrease in the stoichiometric coefficient of the oxidation. The influence of the oxygen concentration in the stream on the intensity of the radiation from the flame has been analysed[56]. Table 3 shows that polystyrene, which is characterised by the lowest degree of completeness of combustion and the greatest radiation from the flame, burns

much more rapidly than other materials. For all polymers except polyoxymethylene, heat transfer to the polymer by radiation predominates; an important role in the combustion process is played by the re-emission of heat from the polymer surface. Because of the large heat losses due to radiation, the flame temperature for polystyrene has the lowest value.

Radiation from the surface also plays an important role in the case of polymers which burn with the formation of carbon. The temperatures in the condensed phase during the combustion of wood under the conditions of a planar counter-current flame have been measured[8]. A temperature of 1870 K is developed on the surface of hot wood with sweeping by an oxidant mixture containing 53% oxygen at a rate of 115 cm s^{-1}. Under these conditions, the chief mechanism of the losses, as in the combustion of coal, is thermal loss by radiation from the polymer surface, which leads to a decrease in the combustion rate. Usually, a temperature of 700–800 K is developed on the surface of wood under fire conditions, and the radiation power can reach 0.6 W cm^{-2}.

VI. MECHANISM OF THE INHIBITION OF DIFFUSION FLAMES BY HALOGEN-CONTAINING INHIBITORS

The diffusion flames of hydrocarbons are convenient model systems for the study of the mechanism of the inhibition of the combustion of polymers in the gas phase. Up to the present, however, there has been no unified view of the nature of the inhibition of diffusion flames of hydrocarbons by various chemical additives. It has been correctly pointed out[57] that the kinetics of a reaction in a flame of a mixture of gases and in a diffusion flame of the same gases are not necessarily identical. The basic difference in a diffusion flame is the existence of zones under the flame and after the flame. The zone under the flame is characterised by a relatively low concentration of oxygen (or its absence), a high concentration of fuel, a sufficiently high temperature, and a diffusion flux of free radicals from the flame. As a result, conditions are created in the region under the flame which are characteristic of gas mixtures rich in fuel, in which various processes are possible, leading to a change in the actual composition of the fuel and the inhibiting additive passing into the flame zone. When the oxidant contains additives, analogous processes of their transformation with the participation of radicals diffusing from the flame zone are possible. This may explain the difference, with respect to the reaction of inhibiting additives, in the behaviour of a diffusion flame and a previously mixed flame.

The action of halogen-containing additives can be considered in detail, since the amount of published data is greatest on this topic. There are two approaches to the explanation of the action of halogen-containing additives in flames—chemical and physical[58]. The chemical approach was first proposed by Fryburg[59]. A typical scheme for the chemical mechanism of inhibition[58] is given below for the addition of HBr to a previously mixed flame, where the radical H$^\cdot$ (O$^\cdot$, OH$^\cdot$) is replaced by the less active radical Br

$$\text{Fuel} + O_2 \rightarrow CO_2 + CO + H_2O + Q$$

Chain propagation and branching

$$OH^\cdot + CO \rightarrow CO_2 + H^\cdot$$
$$OH^\cdot + CH_4 \rightarrow H_2O + CH_3^\cdot$$
$$CH_3^\cdot + O_2 \rightarrow CH_2O + OH^\cdot$$
$$H^\cdot + O_2 \rightarrow OH^\cdot + O^\cdot$$

inhibition:

$$HBr + OH^\cdot \rightarrow H_2O + Br^\cdot$$
$$HBr + O^\cdot \rightarrow OH^\cdot + Br^\cdot$$
$$HBr + H^\cdot \rightarrow H_2^\cdot + Br^\cdot$$
$$HBr + CH_3^\cdot \rightarrow CH_4 + Br^\cdot$$

regeneration of inhibitor

$$Br^\cdot + CH_4 \rightarrow CH_3^\cdot + HBr$$

The efficiency of the action of halogen-containing inhibitors increases in the order F < Cl < Br < I.[58] This provides evidence in support of the chemical mechanism of inhibition. A large number of studies of mixed systems have shown that small quantities of added halogen-containing inhibitors (several mole %) decrease by a factor of ten or more the rate of propagation of the flame and have a marked influence on the limit of flame production[60].

The inhibiting action of halogen-containing compounds is generally related to the formation of the compounds HX (where X is a halogen atom) and their subsequent participation in inhibition according to the scheme given above. It has been pointed out[58], however, that the introduction of small quantities of a halogen-containing inhibitor into a polymer has little influence on the limiting conditions of combustion of the polymer (on the magnitude of the oxygen index OI). A decrease in the OI of the polymer by several units requires the introduction of up to 15–20 mass % of halogen-containing inhibitors[61].

Larsen and Ludwig[58] give data which support the so-called "physical" mechanism of inhibition, that is simple dilution of the hot system by the inhibitor and decrease in the temperature of the flame. Experiments to determine the minimum quantity of inhibitor which must be added to a previously mixed gaseous mixture of air and hydrocarbons to prevent flame propagation in this mixture showed that the concentration of halogen in the mixture is ~70 mass %, irrespective of the type of inhibitor and fuel. F, Cl, Br, and I were found to be equally effective in this comparison, in contrast to the usual method of comparison from the number of moles of inhibitor required for collapse of the flame. These results were confirmed for diffusion flames[62]. Petrella and Sellers[62] determined the concentration of inhibitor from the mass at the combustion limit; the measurements showed that, irrespective of the type of inhibitor (CF_2Cl_2, CF_2ClBr, CF_3Br) and fuel (C_3H_8, n-C_4H_{10}), the halogen concentration was 76.9 ± 2.2 mass %. This result indicates that in a comparison of the concentration of halogens in the flame from the mass, different halogens are almost equally effective, and that the mechanisms of the inhibition coincide to a large extent for mixed and diffusion flames.

The role of halogen-containing inhibitors introduced into a polymer reduces to increasing the mass of polymer which must be gasified to obtain the same fuel flux[58]. A number of studies have shown, however, that it is impossible to attribute the action of inhibitors entirely to an inert diluent, that is to a decrease in the adiabatic temperature of the flame. Thus the efficiency of many inhibitors depends on the total pressure in the system, although a number of exceptions to this rule have been found[63].

Studies of the action on the diffusion flames of halogen-containing inhibitors added to the gas phase are examined below. There are two familiar flame configurations in these experiments—with a parallel stream (Burke–Schumann burner) and with a counter-current of fuel and oxidant.

These configurations differ in the gas-dynamic parameters of the flame. Systems with a parallel stream are characterised by long residence times of the fuel in the zone below the flame, and lower convection in the direction of the flame; in these systems, however, the existence of partial mixing of the fuel with the oxidant at the point of origin of their boundary, that is at the cold wall, is not excluded. In counter-current systems, there is always convection in a direction perpendicular to the flame, which influences the concentration of the reagents and the distribution of temperature in the flame. When allowance is made for these possible differences, the conclusions from the experiments of the two types show fairly good agreement.

The inhibition of diffusion flames by halogen-containing compounds was first studied by Simmons and Wolfhard[64]. The critical concentration of CH_3Br added either with the fuel or with the oxidant, leading to collapse of the flame, was determined under conditions of a coaxial stream of fuel. The number of molecules of inhibitor at which collapse of the flame begins was ~20–30 times smaller when the inhibitor was added with the air than when it was added with the fuel. Studies of the influence of inhibitors on a flame with a coaxial configuration[65,66] confirmed the conclusion[64] that the efficiency of an inhibitor is greater when it is added with the air than when it is added with the fuel.

Friedman and Levy[67] give the dependence of the volume concentration of an inhibitor added with the fuel to a flame at the combustion limit on the rate of flow of the oxidant. In this comparison, the efficiency of the inhibitors decreased in the order $CF_3Br > CH_3Br > CCl_4 > CH_3Cl \gg N_2$. Comparison of the volume concentrations of combustion inhibitors should be supplemented by a comparison of the heat capacities of the fluxes of the gases introduced into the flame, as was done in Ref.58.

The influence of halogen-containing inhibitors on hydrocarbon and hydrogen flames has been studied spectrographically[68]. The introduction of the inhibitor decreases the luminescence of the OH and HCO radicals and increases the luminescence of the C_2 radical and carbon black, and the temperature of the flame decreases with increase in the concentration of the inhibitor.

A counter-current method has been used to compare the efficiency of different inhibitors[69] by determining the dependence of the concentration of inhibitor (mole %) in the air or the fuel required for collapse of the flame on the rate of sweeping of the flame. The fact that in this comparison CF_3Br is slightly more effective than CF_2ClBr, in spite of the higher heat capacity of the latter, indicates that the action of the inhibitors is chemical in character.

The influence of the inhibitor CF_3Br on the diffusion combustion of polymethyl methacrylate and its monomer under conditions of sweeping by a counter-current of the flame has been studied[44]. The inhibitor was introduced with the oxidant. The authors' suggestion that a better model of the diffusion flame of a polymer is obtained when the inhibitor is introduced with the oxidant appears doubtful, since in the combustion of a polymer, an inhibitor moving in the gas phase reacts with the gasified fuel in the zone under the flame. The introduction of CF_3Br into the flame with the oxidant led to the appearance of a luminous flame zone on the fuel side, and the colour of the flame changed from blue to bluish-green. This was due to the radiation of the carbon black and its precursor C_2 (emission in the green range, in accordance with Ref.64). An important result obtained by Seshadri and Williams[44] was the detection of the presence of oxygen at the boundary of a luminous flame. The introduction of an inhibitor into the flame increased the break-through of oxygen into the zone under the flame. The increase in carbon black formation, in the authors' opinion, is due either to the products of the transformation of the inhibitor or an increase in the concentration of oxygen under the flame. The increase in the break-through of oxygen through the flame may be due to a decrease in the temperature of the flame and the consequent decrease in the reaction rate in the flame zone. In the presence of CF_3Br, however, there is practically no decrease in temperature at the combustion limit.

The influence of C_2H_5Br, CCl_4, and $CHCl_3$ on a previously mixed and diffusion counter-current acetylene–air flame has been studied spectrographically[70]. The introduction of inhibitors into a diffusion flame increases in the spectrum the intensity of the emission bands of C_2 and decreases the intensity of the OH bands. The following mechanism has been proposed for the action of Cl-, Br-, and I-containing inhibitors[63]. The inhibitors introduced into the flame increase the formation of carbon black, on whose particles absorption of molecular oxygen can subsequently take place. In fact, this should decrease the concentration of oxygen in the flame and lead to a decrease in the reaction rate, and a decrease in the parameters of the limiting conditions. The authors cited[63] did not observe a change in the concentration of the OH radical in the flame in the presence of inhibitors, and this does not agree with published data. Moreover, their hypothesis that there is a decrease in the oxygen concentration in the flame is not confirmed experimentally and is contradicted directly by the data in Ref.44.

In a number of papers on the combustion of polymers (for example Refs.71–74) it is suggested that halogen-containing inhibitors "operate" in the gas phase in the same way as in gas flames. The action of halogens on combustion was attributed[73,75] to a decrease in the rate of the reactions and a decrease in the flame temperature. However, in Ref.76, which gives data on the combustion of mixtures of polymethyl methacrylate and chlorinated polyethylene, it was established that (in contrast to the gas phase, where Cl plays the role of inert diluent[58]) with the participation of Cl in the degradation processes in the condensed phase, carbon black, apparently formed by the removal of Cl in dehydrochlorination reactions, may accumulate on the polymer surface.

VII. PHOSPHORUS-CONTAINING COMBUSTION INHIBITORS

In addition to compounds of the halogens, compounds of P, B, N, and various metals of the type Sb and As are used as combustion inhibitors. Phosphorus compounds are more frequently used than the others; the possible mechanisms of their effect on the combustion of polymers, formulated in a review[77], are given below.

1. The effect on processes in the condensed phase, an increase in the non-burning residue, and a decrease in the quantity of fuel reaching the flame; the influence on the heterogeneous oxidation of coke.
2. The formation of a surface vitreous or viscous molten layer of high-boiling phosphoric acids, which prevent the processes of diffusion of the fuel and heat transfer.
3. Inhibition of gas-phase reactions.

The specific mechanism of the action of phosphorus-containing fire-proofing agents depends on the nature of the polymers. Thus when introduced into polyethylene, which does not form a residue on degradation, phosphorus compounds operate in the gas phase, but in epoxide compositions they operate by the first two of these mechanisms[78,79]. Some authors suggest that only phosphorus(V) compounds are active inhibitors[77], although other data[80] indicate that

amorphous red phosphorus is also a fire-proofing agent. The efficiency of inhibitors has been related to the way in which they are introduced into the polymer[81].

Analysis of published data shows that although the mechanism of the action of phosphorus-containing compounds in the condensed phase on the whole is not clear, its principal characteristics can be distinguished. Thus in cellulose materials in the presence of fire-proofing agents there is an increase in the yield of carbon as a result of dehydration[1]. Coke is formed according to the following hypothetical scheme:

$$(C_6H_{10}O_5)_x \rightarrow 6xC + 5xH_2O \quad .$$

A gas-phase mechanism of the action of phorphorus compounds in the combustion of polymers has been proposed[81,82]. Thus it has been suggested[82] that in the flame there is heterogeneous destruction of radicals on P_2O_5 particles formed during combustion; this lowers the reaction rate in the flame and leads to a decrease in its temperature.

On the whole, the question of the mechanisms of the action of phorphorus-containing inhibitors remains open. A number of effects have not yet been explained. For example, it has been shown[82] that in spite of the increase in the limiting characteristics of the combustion of polymethyl methacrylate inhibited by phorphorus compounds, the rate of burn-out of the material away from limiting conditions increases. None of the published mechanisms of the inhibition of the combustion of polymers can explain this fact. As noted in a number of publications, in the inhibition of the combustion of polymers by halogen- and phosphorus-containing compounds there is an increase in carbon black formation, smoke formation, or coke formation. Smoky sooty flames are highly luminous, and in them an important role is played by heat transfer by radiation[8]. In the combustion of carbon-forming polymers, a change from a gaseous diffusion flame to heterogeneous oxidation is possible; high temperatures are developed in the upper layer of the condensed phase of the burning polymer[37], and this may also lead to powerful radiation from the surface of the burning polymer.

VIII. CARBON BLACK FORMATION IN THE COMBUSTION OF POLYMERS

The mechanism of the formation of carbon black in diffusion flames is attracting the attention of many research workers[83-92]. A general scheme of the processes leading to the formation of carbon black in flames has been described[1]. Five stages in this process have been distinguished [90]: 1) the formation of nuclei of carbon black (the radicals $C_2^{\cdot}$ and $C_2H^{\cdot}$, polyaromatic radicals) as a result of thermal decomposition reactions in the zone under the flame with the participation of $H^{\cdot}$, $O^{\cdot}$, and $OH^{\cdot}$ radicals from the flame; 2) the formation of larger carbon black nuclei by a mechanism of the radical polymerisation and recombination type; 3) aggregation of the carbon black nuclei to form larger particles; 4) the development of surface growth of the carbon black particles; and 5) heterogeneous burn-out of the carbon black particles in the flame.

Stages 1 and 2 take place by a radical-chain mechanism. In stages 3 and 4, an important role is played by ionic processes[91]. There are other models of carbon black formation, but for these there is less experimental justification[93]. In the last stage, an important role is played by the degree of dispersion of the carbon black formed in the zone under the flame. The more finely dispersed the carbon black, the greater its surface area and the more actively it is oxidised in the flame.

The diffusion flames of methane and ethane at the combustion limit are blue, and carbon black is not formed; with increase in the oxygen concentration in the oxidant, there is an increase in the temperature of the flame, leading to an increase in the thermal decomposition of the fuel and carbon black formation[56]. This effect is also observed in the combustion of polymers, and the degree of completeness of the combustion of the fuel in the flame decreases with increase in the oxygen concentration[94]. The influence of various Br and Cl compounds on the formation of carbon black in diffusion flames of hydrocarbons has been studied[85,86]. Br compounds, when supplied to the diffusion flame with the fuel or with the oxidant, facilitate carbon black formation, but Cl compounds do not lead to any significant increase in carbon black formation. The apparent mechanism of this effect[85] is that the introduction of halogens into the flame lowers the concentration of $OH^{\cdot}$ radicals, and this in turn leads to an increase in the concentration of carbon black nuclei. The participation of the halogen-containing compounds in the stage involving the initiation of carbon black formation is not excluded. A similar effect is observed for various phosphorus compounds, for example $POCl_3$.[95]

IX. MICRO-ENCAPSULATED FIRE-PROOFING AGENTS

The most widely encountered fire-proofing agents, phosphorus- or halogen-containing compounds, are in most cases extremely toxic substances, which volatilise or seep from the material during its processing and use. It is for this reason that in recent years a new and promising method has been developed for introducing fire-proofing agents into polymeric materials in the form of micro-capsules. As a result of micro-encapsulation, the fine particles of liquid, solid, or gaseous fire-proofing agents introduced into a polymer covering are isolated from the surrounding medium, but retain the properties of combustion inhibitors.

By using an appropriate covering material, it is possible to stabilise and even improve the physicomechanical properties of a polymer composition, since the fire-proofing agent in this case simultaneously acts as a modifier. The use of micro-encapsulated fire-proofing agents (MFA) makes it possible to create materials with a working surface enriched in the fire-proofing agent, which increases its fire-resistance without a significant change in the physicomechanical properties. In addition, it becomes possible to use as fire-proofing agents substances which in non-encapsulated form are unsuitable for these purposes, for example water, and also substances with a low boiling point or a high toxicity. Moreover, it is possible to use in micro-encapsulated form fire-proofing agents which in the usual form are incompatible with the polymer matrix.

Micro-encapsulation methods are provisionally classified as chemical and physical. Phase separation methods are based on phase transformations in polymer solutions. The encapsulated substance is dispersed in the polymer solution, after which phase separation is initiated by changing the temperature, the pH of the medium, or the concentration of the components. As a result, the polymer separates from solution and is adsorbed on the particles of encapsulated substance, forming a micro-covering round them. Polymer encapsulation methods are based on the polymerisation or polycondensation of monomers or pre-polymers on the particles of the substance being encapsulated. Physical methods of micro-encapsulation use centrifuges, spray apparatus, etc. Phase separation and polymerisation methods are usually employed for the micro-encapsulation of fire-proofing agents.

The best known fire-proofing agent, containing phosphorus and halogen atoms, is tris(2,3-dibromopropyl) phosphate

$$(BrCH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_2—O—)_3—PO$$

which is a toxic liquid, obtained by brominating allyl alcohol and the subsequent reaction of the 2,3-dibromopropanol with $POCl_3$. This is one of the most widely encountered fire-proofing agents, used for polyalkenes, polyesters, polyurethanes, and polystyrene[96]; a number of methods for its micro-encapsulation have been patented[96–101]. The micro-capsules are obtained by aqueous-phase separation (covering material melamine–formaldehyde[97], urea–formaldehyde[97], polysiloxane[100], dextrin[96]) or by polymerisation, again in an aqueous medium (covering material polyurethane[98–100] or copolymers of ethylene with methacrylyl chloride[100] or of styrene with divinylbenzene[101]). Micro-capsules of tris-(2,3-dibromopropyl) phosphate have been used in fire-resistant carpets[97], paints, and polyurethane foam[102,103], and to impregnate fabrics to increase their fire resistance[100].

Methods for the micro-encapsulation of tris(2,3-dichloropropyl) phosphate[98,99], tris(1-chloro-3-bromoisopropyl) phosphate[101], and tris(1-bromo-3-chloroisopropyl) phosphate[101] have been patented. Methods have also been described for micro-encapsulating tricresyl phosphate, red phosphorus, ammonium phosphate, and other phosphorus-containing compounds. Tricresyl phosphate, an oily liquid, is micro-encapsulated in polyurethane[98,99,101], polymethyl methacrylate[101], and gelatin[104] coverings. Red phosphorus, which has found extensive application as a fire-retarding agent in many polymeric materials, has the disadvantage that at the temperatures of the processing of plastics in the presence of residual moisture it is capable of forming the toxic phosphine. The use of this fire-proofing agent in micro-encapsulated form prevents the formation of phosphine; a number of methods exist for the micro-encapsulation of red phosphorus[105–108].

When 10% of micro-encapsulated phosphorus is introduced into a polymer, the OI of the polyamide† increases by five units, and that of polyterephthalate, polypropylene, and polystyrene by approximately two units[106].

Of the halogen-containing fire-proofing agents, compounds containing chlorine and bromine have been most widely used. Bromine-containing compounds are generally more effective, although they are more toxic[96]. On the one hand, they bring about better initiation of the decomposition of the polymer chain, and on the other hand the hydrogen halides formed in the region before the flame are inert diluents and lower the flame temperature. Moreover, halogens can intensify carbon black formation in the flame. The following are now used in micro-encapsulated form: 1,1,2,2-tetrabromoethane[96,97,99] to obtain self-extinguishing polyurethane foam, 1,2-dibromoethane[96], and chloroalkanes containing 12–72% chlorine[102,110], which are used as fire-extinguishing additives to polyalkenes, polystyrene, natural rubbers, etc.

Micro-encapsulation makes it possible to use as fire-proofing agents substances which cannot be used at all in non-encapsulated form. These are primarily compounds with a low boiling point—Freons and low-boiling hydrocarbons. Methods have now been developed for micro-encapsulating tetrafluorodibromoethane, trichlorotrifluoroethane, and tetrachlorodifluoroethane, by aqueous-phase separation[103,111].

†The OI was determined by the published method[109].

The micro-encapsulation of water and aqueous solutions of fire-proofing agents is of particular interest. The method of phase separation in ternary water–oil–water emulsions and the method of interphase condensation and polymerisation are most frequently used for these purposes. Water is micro-encapsulated in the form of dilute solutions of salts such as sodium and potassium aluminates, borates, etc.[112–122] to obtain a stable double covering, or in the form of concentrated solutions of water-soluble fire-proofing agents (ammonium phosphates, chloride, and bromide). Micro-encapsulated water or its solutions are used as filler to decrease the combustibility of fibres, films, etc. The micro-capsules obtained, with diameter ~5 μm, contain 68 to 75 mass % water, and its concentration remains unchanged after treatment under normal conditions for one week or on heating to 100 °C for 1 h;[20] the external appearance of the micro-capsules also remains unchanged.

The conditions of the processing of polymeric compositions containing MFA (temperature, pressure) should be such that the covering of the micro-capsules does not break down in the process. The material of the covering should be inert with respect to the components of the polymer composition, or should react with the polymer or its components, leading to an increase in the strength of the coverings of the micro-capsules and in the strength of their attachment to the polymer.

The addition of polystyrene micro-capsules containing water or sodium metaphosphate has been recommended for the production of fire-resistant polyurethane[119]. Micro-encapsulated Freon-113 has been recommended for this purpose[123]. A method has been developed for obtaining fire-resistant cast polymer compositions containing an encapsulated inorganic filler and micro-capsules containing water[124]. These compositions are used to prepare plastics with a high mechanical strength, which can be used as constructional materials.

The migration of a fire-proofing agent from a polymer matrix has been studied in specimens containing dextrin micro-capsules with a 90% concentration of 1,1,2,2-tetrabromoethane[96]. When the specimens were kept at 100° for 20 h, the concentration of MFA decreased by 5%, and that of the non-encapsulated fire-proofing agent decreased by 99% (that is it volatilised practically completely).

The combustibility of an epoxide binding agent based on ED-20 epoxide resin, hardened by polyethylene polyamine and containing MFA, has been studied[125]. The fire-proofing agents used were tris(2,3-dibromopropyl) phosphate and Freon-$318B_2$ (polyvinyl alcohol covering). Micro-capsules with a diameter smaller than 200 μm were used; the mass fraction of the fire-proofing agent in the micro-capsules was 85–98%. Estimation of the fire-extinguishing action of the fire-proofing agents studied[125] showed that their efficiency decreases in the order: tris(2,3-dibromopropyl) phosphate > Freon-$318B_2$ > Freon-$114B_2$. The value OI = 40 is reached on the addition of 50, 60, or 70 mass % of these additives respectively, and the limiting oxygen concentration c_{lim} = 40% is reached for 65–74 mass % of the additive. The action of tris(2,3-dibromopropyl) phosphate as an MFA is shown in the condensed phase in the same way as in the case of the non-encapsulated fire-proofing agent[126].

To determine the mechanism of the action of MFA, the influence of the type of fire-proofing agent, the material of the covering, and the size of the micro-capsules on the temperature at which they open in pure form and in a polymer matrix was studied[127–129], and the efficiencies of the action of fire-proofing agents added to the polymer matrix in the free form and as micro-capsules were compared. The fire-proofing agents studied were carbon tetrachloride,

trichloroethyl phosphate, tris(2,3-dibromopropyl) phosphate, Freons 114-B_2 and 318-B_2, water, etc. Polyvinyl alcohol, gelatin, and polyurea were used as the covering of the micro-capsules, and an epoxide matrix was usually employed as the polymer matrix.

At a heating rate of 10 K s^{-1}, the temperature at which the micro-capsules open coincides with the temperature at which intensive decomposition of the material of the covering begins. Irrespective of the type of fire-proofing agent and the size of the micro-capsules, the temperatures at which they open for coverings of polyvinyl alcohol, polyurea, and gelatin are 210–240, 200, and 70–85° respectively[129], and the range of temperatures in which opening of 80% of the micro-capsules of fractions of the same size takes place does not exceed 10 K.

Fire-proofing agents can be divided into two classes, according to the type of opening of the micro-capsules. The first class consists of low-boiling liquids such as Freons, CCl_4, H_2O, etc., which are characterised by the fact that at the moment of opening, the liquid in the covering is greatly superheated, and when the opening temperature of the micro-capsules is reached they "explode", accompanied by a sharp decrease in the mass of the specimen; the second class consists of high-boiling liquids [fire-proofing agents such as tris(2,3-dibromopropyl) phosphate, trichloroethyl phosphate, etc.] or solid substances. A characteristic feature of MFA of the second class is that with increase in the temperature of the specimen, a smooth decrease in its mass takes place.

The mechanism of action of fire-proofing agents of the second class, added to a polymer matrix, will be considered first. When the material is heated, the micro-capsules open, and the fire-proofing agent is transferred to the polymer melt in the surface layer of the specimen. The presence of the fire-proofing agent in the thermal decomposition zone intensifies the process of carbon formation on the surface of the burning polymer, and this in turn leads to a change in the conditions of heat and mass exchange between the polymer surface and the flame. When the thermal balance is broken down, the combustion of the polymer stops. With increase in the concentration of the fire-proofing agent there is a smooth increase in the OI. The efficiency of MFA of this class is the same as that of the same fire-proofing agents in the free state. A significant increase in the OI values for these systems can be obtained only by adding large quantities of fire-proofing agent (up to 30–40 mass %) to the polymer composition. The addition of this quantity of fire-proofing agent in the free form is not possible, since it would seep from the polymer matrix; the use of MFA solves this problem.

For MFA of the first class, for which the opening of the covering of the micro-capsules is accompanied by critical phenomena ("micro-explosions"), the liquid at the moment of opening of the micro-capsules is highly superheated. The stable superheated state of the liquid inside the covering is apparently due to the absence of nuclei for vapour formation. When the decomposition temperature of the material of the covering is reached, defects are produced in it, leading to breakdown of the micro-capsule. The "micro-explosion" which accompanies the breakdown of the micro-capsule is stronger, the greater the superheating of the liquid. If the liquid in the capsule is not superheated and its boiling point is higher than the temperature at which the material of the covering begins to decompose, gradual decomposition of the latter takes place, with slow evaporation of the liquid.

Fig.2 shows that the addition of low concentrations of a low-boiling MFA to the polymer does not lead to a change in its decomposition temperature. A sharp decrease in the temperature at which decomposition starts takes place at a concentration of ~2 mass % MFA in the specimen. At this concentration, the so-called dispersion effect begins to appear. The size of the dispersed particles of the polymer and the rate of their removal depend on the strength of the "micro-explosion". In the "micro-explosion", the particles of the polymer are torn from the main mass and removed from the flame zone, without burning. For an increase in the MFA concentration by more than 3%, the temperature of the start of the decomposition remains constant and equal to the temperature at which the degradation of the covering of the micro-capsule begins, and is independent of the type of matrix[129].

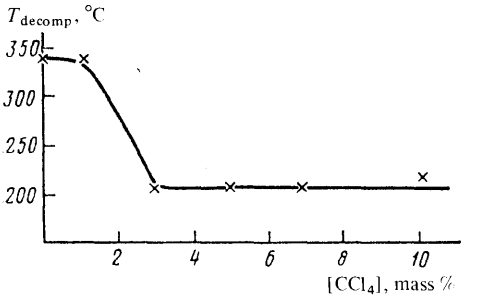


Figure 2. Influence of the concentration of micro-encapsulated fire-proofing agent (CCl_4) on the temperature of the start of the decomposition of the polymer matrix T_{decomp}.[129]

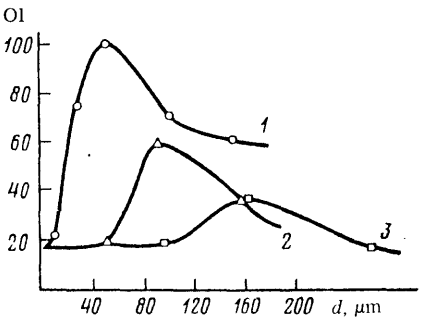


Figure 3. Influence of the size of the micro-capsules (d) and the type of MFA on the efficiency of the inhibition of the combustion of the epoxide composition ED-20 + polyethylenepolyamide: *1*) CCl_4, *2*) Freon-318B_2, *3*) Freon-114B_2, MFA concentration 7 mass %.[128]

A study of the combustibility of epoxide polymers in the presence of MFA using the published methods for determining the OI [109] and for estimating the minimum ignition

energy[130] showed that with increase in the percentage dispersion of the polymer there is an increase in its OI and ignition temperature, that is a decrease in the degree of combustibility. It was also established that the size of the micro-capsules has a significant influence on the efficiency of the decrease in the combustibility of the polymer in the presence of the MFA (Fig.3), and the maximum value of the OI is observed for different diameters of the micro-capsules, depending on the type of fire-proofing agent[127]. In spite of the complexity of the physical mechanism of their action, the use of fire-proofing agents in micro-encapsulated form provides an extremely effective method for reducing the combustibility of polymeric materials, and there is no doubt that the development of this field of the chemistry and technology of polmers is promising.

Thus an analysis of the data given in the present review indicates that in the development of methods for decreasing the combustibility of polymers it is necessary to pay particular attention to the structure of the polymer and the interaction of the inhibitor with the polymer and to take account of the reactions involved in the degradation in the condensed phase of the polymer and the inhibitor and the transformations in the gas phase.

Published data indicate the following principal ways of reducing the combustibility of polymers: 1) the addition of carbon-forming catalysts to the polymer. Depending on the type of polymer, these may be metal salts, phosphorus-containing compounds, halogen-containing compounds with antimony oxide, etc. When carbon is formed on the surface of a burning polymer, there is a deterioration in the heat and mass exchange between the flame and the polymer surface and a decrease in the flow of fuel into the flame zone, and the flame is extinguished; 2) the use of polymers combined with non-combustible materials with a high heat capacity and heat conductivity (filled, or in constructions); 3) the addition to the polymer of additives whose thermal decomposition adds inert diluents to the gas phase, decreasing the temperature of the flame and leading to its extinction; and 4) the addition to the polymer of additives whose decomposition leads to the appearance in the gas phase of active inhibitors of the gas-phase oxidation reactions (bromine-containing compounds are the most effective), again leading to collapse of the flame.

A new trend, namely the use of micro-encapsulated fire-proofing agents, is very interesting and promising. In this case, there are several simultaneous effects: dispersion of the polymer from the surface, leading to a decrease in the degree of combustion of the polymer (up to 50 mass % of the polymer is removed from the flame zone); physical dilution of the flame, leading to a decrease in its temperature; and chemical inhibition of the reactions in the flame in the case of the micro-encapsulation of effective gas-phase inhibitors.

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Institute of Chemical Physics,
Academy of Sciences of the USSR,
Moscow

Translated from *Uspekhi Khimii*, 53, 347-365 (1984) U.D.C. 541.128.34

New Advances in the Chemistry of Methane

E.A.Grigoryan

The review deals with new reactions of methane in the presence of organometallic catalysts. The available data on deuterium-hydrogen exchange between methane and the methyl groups of the catalyst and on the reactions involving the addition of methane to low-valence transition metal complexes and to unsaturated hydrocarbons are surveyed. Certain other aspects of the chemistry of methane of theoretical and applied interest are considered.
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I. INTRODUCTION

Petroleum processing products constitute at present the main raw material source for the preparation of the majority of organic compounds and polymeric materials. This is the reason for the continuing increase in the rate of extraction and processing of petroleum during the last decades, which has led to the danger of exhaustion of its available resources. According to the estimates of specialists, if the present rate of development of the petroleum processing industry is maintained, the world petroleum reserves will be virtually completely exhausted after 30–40 years. The continuously increasing deficiency of petroleum and petroleum products is already facing chemists with the task of creating a new raw material source for the manufacture of organic substances and polymeric materials.

In nature there are two sources available for organic chemistry, with enormous reserves still available, namely coal and natural gas. The possibility, in principle, of obtaining hydrocarbon raw materials and natural liquid fuel from coal has been known for a long time but the imperfection of the coal processing technology, the severe conditions required for this purpose, and other, including purely economic, factors have created serious obstacles to the realisation of this process in industry. The conversion of natural gas into a hydrocarbon raw material, for example, the preparation of acetylene, have long been achieved on an industrial scale. These processes also proceed at high temperatures and pressures with very low yields and very low selectivity.

On the other hand, it is well known that enzymes exist in nature which oxidise methane (the principal component of natural gas) to methanol under the usual conditions with a high selectivity. The progress in the chemistry of alkanes in recent years is due to the endeavour to create new highly efficient and selective ways of processing natural gas.

The work of Enikolopov and Nalbandyan has made an enormous contribution to the development of the chemistry of saturated hydrocarbons. As early as the 1950's, they investigated in detail the kinetics and mechanism of the gas-phase oxidation of methane by molecular oxygen[1-19]. Since these classical studies have been described in detail in other reviews and monographs[19-21], in the present article the gas-phase reactions of methane will not be considered.

The activation of alkanes under mild conditions in the presence of soluble platinum complexes was first observed by Shilov and co-workers in 1969.[22] It was established, in particular, that the activation of the C–H bond in alkane can lead to deuterium–hydrogen exchange involving the alkanes and their chlorination or oxidation[23-26]. The publication of these studies attracted much interest to the chemistry of paraffinic hydrocarbons and new catalysts for the activation of the CH bonds in saturated hydrocarbons, mainly based on the complexes of Group VIII elements, were soon discovered [27-30].

Comparative analysis of the physicochemical characteristics of hydrogen, methane, ethylene, and other hydrocarbons indicates the possibility of employing Ziegler–Natta organometallic catalysts for the activation of the C–H bonds in the methane molecule. Table 1 presents the bond energies D, the ionisation potentials IP, the electron affinities EA, and the proton affinities PA of methane, hydrogen, ethylene, acetylene, and benzene[26]. It is seen that the C–H bond energy in methane is approximately the same as the H–H bond energy in the hydrogen molecule, but is lower than the C–H bond energies in acetylene, benzene, and ethylene. The ionisation potential of methane is higher than those of benzene, ethylene, and acetylene, but is lower than the ionisation potential of hydrogen. Methane has a smaller proton affinity than benzene and ethylene but higher than hydrogen.

In terms of the characteristics considered, methane thus occupies an intermediate position between hydrogen and ethylene. This factor led to the hypothesis that the activation of methane and its chemical reactions can be achieved in the presence of catalysts capable of activating hydrogen and ethane molecules, although methane should then manifest a lower reactivity than hydrogen owing to steric hindrance. The hydrogenation catalysts and olefin polymerisation catalysts of the Ziegler–Natta type are known to belong to this class.

Table 1. The physicochemical characteristics of hydrocarbon and hydrogen molecules[26].

Molecule	D(R-H), kcal mol^{-1}	IP, eV	EA, eV	PA, eV
H_2	104	15.4	−3.60	4.4
CH_4	104	12.7	—	5.3
C_2H_4	106	10.5	−1.81	6.9
C_6H_6	109	9.2	−1.10	7.5
C_2H_2	120	11.4	—	—

When hydrogn interacts with organometallic catalysts of this type under the usual conditions, the transition metal (M)–carbon bond undergoes hydrogenolysis:

$$M{-}R + H_2 \rightarrow M{-}H + RH \quad .$$

In the absence of the monomer, the reaction results in the evolution of alkane and the formation of a transition metal hydride derivative. In addition, it has been shown[31] that, under these conditions, D_2 molecules enter into deuterium–hydrogen exchange with the alkyl groups of the catalyst. The hydrogenolysis of the M–C bond plays a decisive role also in the hydrogenation reactions of unsaturated hydrocarbons. Analogous reactions of methane with organometallic catalysts have been observed recently for the first time.

Deuterium–hydrogen exchange reactions in methane, the addition of methane to unsaturated hydrocarbons and low-valence transition metal complexes, and reactions involving the exchange of alkyl groups between alkanes and organometallic complexes of 3*d* transition elements have been discovered in recent years. These reactions are especially interesting, because they proceed under mild conditions and in non-polar solvents such as heptane and benzene.

This review describes in detail the studies by Enikolopov's school on the activation of methane in the presence of organometallic complexes in hydrocarbon media and analyses the causes of the relatively high reactivity of methane compared with heavier homologues.

II. THE INTERACTION OF DEUTEROMETHANE WITH ZIEGLER–NATTA CATALYSTS

The interaction of methane can be conveniently studied in the presence of Ziegler–Natta catalysts in which far-reaching transformations of the system components, leading to the reduction of the transition metal with evolution of gaseous products, do not occur. It is therefore useful to employ catalytic systems containing organoaluminium components which have the weakest reducing properties but can alkylate transition metal compounds. It is known[32] that such requirements are met fairly satisfactorily by dimethylaluminium chloride. Its interaction with transition metal salts results in the formation in most cases of an alkylated complex exhibiting catalytic activity and stable in the absence of monomers[33].

The interaction of deuteromethane with catalytic systems based on titanium tetrachloride, biscyclopentadienyltitanium dichloride, diacetylacetonatiotitanium dichloride, vanadium trichloride, and vanadium triacetylacetonate in combination with dimethylaluminium chloride has been investigated in the temperature range 20–70 °C and in the pressure range 0.4 to 10 atm.[34] The results of the mass-spectrometric analysis of the products have shown that the interaction of deuteromethane with the above catalysts results in deuterium–hydrogen exchange between methane and the alkyl groups of the catalytic system. Dideuteromethane is then formed preferentially; however, mono- and tri-deuteromethane are also found in the products together with CH_2D_2. It is noteworthy that, in the presence of deuteromethane, fairly large amounts of methane are found in the gas phase. Fig.1 shows that the amount of methane in the gas phase increases with time almost linearly, while the accumulation of di- and trideuteromethane takes place after an appreciable induction period. The evolution of methane evidently occurs in the stage involving the formation ot the active centres responsible for the deuterium-hydrogen exchange.

The accumulation of methane in the presence of deuteromethane can be caused by the reversibility of the intramolecular or intermolecular disproportionation of the methyl groups bound to the transition metal atom:

$$\rangle M\langle^{CH_3}_{CH_3} \rightleftarrows M{=}CH_2 + CH_4 \quad ;$$

$$2\,\rangle M{-}CH_3 \rightleftarrows \rangle M{-}CH_2{-}M\langle + CH_4 \quad .$$

The formation of carbene complexes in such systems has now been rigorously demonstrated[35,36]. In the catalytic systems investigated these equilibria are apparently displaced largely to the left under the usual conditions. The hypothesis of the reversibility of the disproportionation of the alkyl groups[34] makes it possible to explain not only the accumulation of methane in the presence of an excess of deuteromethane but also the formation of di- and tri-deuteromethanes. Indeed the addition of deuteromethane to the carbene complexes of transition metals should lead to the formation of deuteromethyl derivatives whose disproportionation leads to the formation of di- and tri-deuteromethanes, for example, in accordance with the mechanisms

$$\rangle M{=}CH_2 + CD_4 \rightarrow \rangle M\langle^{CH_2D}_{CD_3} \rightarrow \begin{cases} \rangle M{=}CD_2 + CH_2D_2 \quad ; \\ \rangle M{=}CHD + CHD_3 \quad ; \end{cases}$$

$$\rangle M{-}CH_3 + 2CD_4 \rightarrow 2\,\rangle M{-}CD_3 + CH_2D_2 \quad .$$

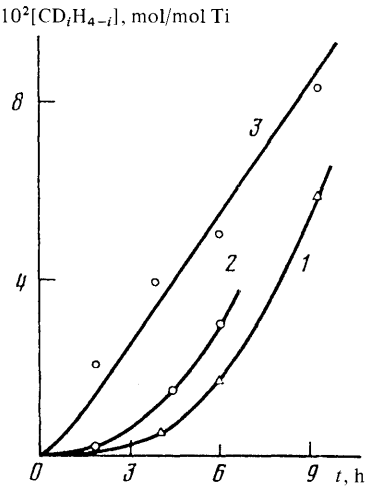


Figure 1. Kinetics of the deuterium–hydrogen exchange between CD_4 and the $TiCl_4$–$Al(CH_3)_2Cl$ catalytic system[34]: 1) dideuteromethane; 2) trideuteromethane; 3) methane; 20 °C, 3 atm, $[TiCl_4] = 5 \times 10^{-2}$ M, Al/Ti = 4.

The formation of monodeuteromethane can be readily explained by taking into account the possibility of the exchange of the methyl groups bound to the transition metal and the aluminium atom[37]; however, the possibility of the direct interaction of deuteromethane with the transition metal complex containing the M–CH_3 σ-bond is of greatest interest[34]:

$$\rangle M{-}CH_3 + CD_4 \rightarrow \rangle M{-}CD_3 + CH_3D \quad .$$

This reaction, which takes place most readily in the case of vanadium catalysts, is analogous to the hydrogenolysis of the M–C σ-bond.

It must be emphasised that the interaction of gaseous deuterium with the $TiCl_4$–$Al(CH_3)_2Cl$ system under identical conditions also results in the formation of the same deuteromethanes as in the reactions of deuteromethane with this system (Table 2)[31]. The identical proportions of the deuteroproducts in the interaction of gaseous deuterium and deuteromethane with Ziegler–Natta catalysts indicates the similarity of the mechanisms of the activation of the hydrogen and methane molecules in the coordination sphere of the transition metal. In the presence of small amounts of pyridine the deuterium–hydrogen exchange involving methane is fully suppressed. Evidently pyridine enters into the coordination sphere of the transition metal, forming a stable complex and preventing thereby the coordination and activation of methanes.

Table 2. The yields Q of the gaseous products of the interaction of deuterium with the $TiCl_4$–$Al(CH_3)_2Cl$ catalytic system[31]*.

τ, h	10^2Q, mol/mol Ti			
	CHD_3	CH_2D_2	CH_3D	CH_4
2	0.2	0.1	0.4	2.3
4	0.4	1.7	0.3	3.6
8	1.9	6.5	—	11.0
10	2.9	7.2	—	14.7

*Solvent—heptane; 50 °C; $[TiCl_4] = 2.5 \times 10^{-2}$ M; Al/Ti = 4.

The validity of the above ideas about the mechanism of the interaction of deuteromethane with Ziegler–Natta catalysts has been confirmed by the results of mass-spectrometric analysis of the gaseous products of the hydrolysis of the catalytic system where mono-, di-, and tri-deuteromethanes were detected[34]. The formation of deuterated methyl groups in the catalytic systems is possible only as a result of the activation of the C–D bond in the deuteromethane molecule when the latter interacts with the active centres of the catalyst. Thus the above results indicate the activation of the methane molecule in the coordination sphere of the transition metal.

The proposed mechanism of the deuterium–hydrogen exchange presupposes two possible pathways in the interaction of methane with organometallic complexes: (1) the reaction which is the reverse of the disproportionation of alkyl groups and (2) the exchange of alkyl groups between methane and the organometallic compound. Recently it has been possible to obtain direct evidence for the possibility of the occurrence of that reaction with participation of methane.

III. THE ACTIVATION OF METHANE BY LOW-VALENCE TRANSITION METAL COMPOUNDS

The disproportionation of alkyl groups containing a β-carbon atom in dialkyl compounds of transition metals proceeds via the scheme

$$\rangle M\langle^{C_2H_5}_{C_2H_5} \rightarrow \rangle M + C_2H_6 + C_2H_4 ,$$

according to which the oxidation state of the metal changes at once by two units and an alkane and an alkene are formed[33,37].

A reversible reaction can be achieved in the oxidative addition of an alkane to a complex of a transition metal in a low oxidation state. The analogous reaction with hydrogen is well known and takes place under the usual conditions at a high rate, for example, in the hydrogenation of olefins[38]:

$$\rangle M + H_2 \rightarrow \rangle M\langle^{H}_{H} \xrightarrow{C_2H_4} \rangle M\langle^{H}_{C_2H_5} \rightarrow \rangle M + C_2H_6 .$$

It is easy to estimate that the oxidative addition of methane should be less exothermic by ~10 kcal mol^{-1} than the addition of hydrogen. Steric hindrance may be an additional obstacle in the case of methane.

The oxidative addition of methane to low-valence transition metal complexes should entail the formation of alkyl hydride derivatives:

$$\rangle M + CH_4 \rightleftarrows \rangle M\langle^{H}_{CH_3} .$$

Under the usual conditions, this equilibrium is known to be displaced to the left[39], so that the isolation of the product of the oxidative addition of methane is not a simple task and the occurrence of the reaction can be inferred only from the results of the study of isotope exchange involving methane.

The possibility of the oxidative addition of alkanes to platinum(II) has been postulated by Shilov and co-workers[26]. Recently the same workers were able to isolate and investigate the σ-aryl complexes of platinum(IV) from a solution of hexachloroplatinic acid and hydrocarbons in a CF_3COOH + H_2O mixture, although the mechanism of the formation of the Pt–R bond was not rigorously demonstrated[40–44].

It has been established[45–47] that deuterium–hydrogen exchange between methane and deuterium takes place in a benzene solution of vanadocene (Cp_2V), leading to the formation of CH_3D, CH_2D_2, CHD_3, and CD_4 in the proportions 1.0 : 0.2 : 0.3 : 0.12. The yield of deuteromethanes (for a methane content in the initial mixture of 35% and a pressure of 250 mmHg) after 24 h is 2–6%. Here one should note that repeated deuteration of the solvent (benzene) takes place simultaneously with formation of hexa- and penta-deuterobenzenes.

The formation of methanes deuterated to different extents in the isotope exchange between D_2 and CH_4 may be due to the oxidative addition of methane, for example, via the mechanism

$$\rangle M + CH_4 \rightleftarrows \rangle M\langle^{H}_{CH_3} ;$$

$$\rangle M\langle^{H}_{CH_3} + D_2 \rightarrow \begin{cases} \rightleftarrows \rangle M\langle^{D}_{CH_3} \rightleftarrows \rangle M\langle^{H}_{CH_2D} \\ \rightarrow \rangle M\langle^{H}_{D} + CH_3D \end{cases} .$$

The preferential formation of monodeuteromethane may be associated with the simultaneous occurrence of the oxidative addition of deuterium:

$$\rangle M + D_2 \rightarrow \rangle M\langle^{D}_{D} \xrightarrow{CH_4} \rangle M\langle^{D}_{H} + CH_3D .$$

The oxidative addition of methane becomes thermodynamically more favourable when the process is accompanied by the simultaneous rupture of the double bond in the olefin (for example, ethylene) molecule in the coordination sphere of the metal. In this case a methyl derivative should be formed in which the disproportionation reaction, leading to

the reformation of methane and ethylene, is faciliated:

$$>M\leftarrow\overset{CH_2}{\underset{CH_2}{\|}}+CH_4\rightleftarrows >M\langle^{CH_3}_{C_2H_5}\,.$$

On the other hand, if one of the hydrocarbons contains deuterium atoms, the reversibility of this reaction leads to deuterium–hydrogen exchange between methane and ethylene.

Table 3. The products of the deuterium–hydrogen exchange between C_2D_4 and CH_4 under the influence of Cp_2V.[45]*

C_2D_4/CH_4	Yield, mol/mol Cp_2V								
	C_2HD_3	C_2HD_2	C_2H_3	C_2H_4	CHD_3	CH_2D_2	CH_3D	C_6D_6	C_6D_5H
0.88	—	—	0.2	33.5	0.5	2.4	—	30.2	4.1
0.34	0.1	0.9	—	10.7	0.7	—	1.6	6.4	1.5

*Solvent—benzene; 70 °C; 40 atm; 100 h; $[Cp_2V] = 3.5 \times 10^{-2}$ M.

Table 4. The multiple deuterium–hydrogen exchange factor (M) in the $Cp_2V + CH_4 + C_2H_4 + C_6H_6$ system at 70 °C.[47]

Amount of initial hydrocarbon			$10^3\cdot[Cp_2V]$, M	τ, h	Deuterating agent	M		
$10^3[CH_4]$, mol	$10^3[C_6H_6]$, mol	$10^3[C_2H_4]$, mol				CH_4	C_6H_6	C_2H_4
23.70	112.50	20.78	35.4	100	C_2D_4	2.2	5.9	3.9
43.62	112.50	15.04	35.4	100	C_2D_4	1.1	5.8	3.8
15.36	107.0	18.00	30.7	80	CD_4	2.0	5.8	4.0
6.92	123.0	9.17	11.7	80	CD_4	1.0	4.5	4.0
13.40	56.25	18.05	32.0	80	C_6D_6	2.3	4.5	3.7
56.70	56.25	—	73.0	44	$(C_5D_5)_2V$	0	4.2	—
9.17	56.25	17.5	73.0	44	$(C_5D_5)_2V$	0	0	2.3
—	112.5	32.0	35.4	100	C_2D_4	—	5.9	—

Table 3 presents data for the isotope exchange between methane and ethylene in the presence of vanadocene at 70 °C. Evidently benzene is also involved in the exchange reaction and in the methane–deuteroethylene–benzene system the deuterium–hydrogen exchange results in the formation mainly of fully deuterated benzene and "light ethylene", while methane gives rise to simple exchange products. Table 4 shows that the multiple deuterium–hydrogen factor is on average 1.7 for methane, while under the same conditions it reaches 5.9 for benzene and 4.0 for ethylene[47].

It follows from the data of Shestakov et al.[47] presented in Table 5 that less than 10% of the benzene employed and up to 44% of the ethylene participate in the deuterium–hydrogen exchange reactions. On this basis, one may claim that in the presence of Cp_2V the benzene and ethylene molecules are involved in multiple exchange reactions.

The deuterium–hydrogen exchange between methane and benzene in the absence of ethylene proceeds much more slowly. This fact together with the results of the study of the H–D exchange in the C_2D_4–CH_4–C_6H_6, C_2H_4–CD_4–C_6H_6, and C_2D_4–C_6H_6 systems (Tables 5 and 6) shows that benzene is deuterated as a result of its reaction with deuteroethylene, while methane is involved in exchange with ethylene in a parallel pathway[46].

In the C_2H_4–CD_4–C_6H_6 system the ethylene molecule transfers deuterium atoms from methane to benzene. Indeed the rate of deuteration of benzene in this system is much higher than in the system where the deuterating agent is deuterethylene and the multiple exchange factor is the same in both cases.

Table 5. The yields of deuterohydrocarbons and the specific rates of isotope exchange ν_{sp} in various systems in the presence of vanadocene[47].

System	Amount of hydrocarbons involved in exchange, mole %			$10^2\nu_{sp}$, litre $mol^{-1}h^{-1}$		
	methane	benzene	ethylene	methane	benzene	ethylene
C_2D_4–CH_4–C_6H_6	2.5	7.8	43.8	11.9	11.4	44.3
	0.7	2.4	26.2	5.2	4.2	20.2
C_2D_4–$^{13}CH_4$–C_6H_6	0.6	1.7	—	11.9	9.4	—
C_2H_4–CD_4–C_6H_6	0.8	0.1	11.0	24.1	1.1	24.8
C_2H_4–CH_4–C_6D_6	2.0	0.5	4.5	16.4	1.0	4.8
C_2D_4–C_6H_6	—	3.7	0.5	—	6.3	39.4
C_6H_6*	—	0.002	—	—	0.1	—
C_2H_4–CH_4–C_6H_6*	0	0	0.05	0	0	3.7

*The experiments were performed in the presence of $(C_5D_5)_2V$.

Table 6. The specific rates and the multiple deuterium–hydrogen exchange factors in the $CH_4 + C_2D_4 + C_6H_6$ system in the presence of various metallocenes[45–47]*.

Catalyst	M			$10^2\nu_{sp}$, litre $mol^{-1}h^{-1}$		
	CH_4	C_6H_6	C_2H_4	CH_4	C_6H_6	C_2H_4
Bz_2Ti	2.6	4.9	3.0	40.1	91.4	14.8
Cp_2V	2.2	5.9	3.9	11.9	11.4	44.3
Cp_2Mn	1.1	4.8	3.5	1.1	7.9	9.0
Cp_2Fe	1.0	4.9	3.5	0.1	1.5	6.0
Cp_2Co	1.0	4.7	2.9	0.3	0.3	5.0
Cp_2Ni	1.0	4.7	3.0	0.2	0.1	0.5

*Solvent—benzene; 70 °C; 2.5 atm; 100 h.

Presumably the formation of deuterocarbons is due to their metathesis reaction involving the dissociation of the C=C double bond in ethylene. Indeed the methyl hydride complex formed in the oxidative addition of methane[26,45] can be converted into a carbene complex[48], which is the active centre of metathesis according to the authors[49]. The formation of deuterated hydrocarbons can then be represented schematically as follows:

$$>M+CH_3\rightleftarrows \underset{H}{\overset{|}{>M}}\langle^{CH_3}_{H}\rightleftarrows >M{=}CH_2+H_2\,,$$

$$\underset{D_2C=CD_2}{\overset{M=CH_2}{\diagup\!\!\diagdown}}\longrightarrow >M{=}CD_2+H_2C{=}CD_2\,.$$

When [^{13}C] methane was used, the transfer of carbon-13 atoms to the ethylene molecules should have been observed: however, mass-spectrometric studies showed that the interaction of the C_2H_4, $^{13}CH_4$, and C_6H_6 hydrocarbons with Cp_2V

does not lead to the isotope exchange of carbon between the system components[47]. The replacement of methane by [^{13}C]-methane hardly affects also the rate and degree of the deuterium–hydrogen exchange between deuteroethylene and methane. These data show that in the system investigated there are no metathesis reactions and that the hydrocarbons are deuterated due to the isotope hydrogen–deuterium exchange.

It is noteworthy that, on passing from benzene to deuterobenzene or from methane to deuteromethane, the rate of deuterium–hydrogen exchange with ethylene falls appreciably other conditions being equal. The kinetic isotope effect k_H/k_D is 3.6 for benzene and 3.1 for methane. The occurrence of a significant isotope effect confirms that the dissociation of the C–H bond in the benzene and methane molecules takes place in the rate-determining stage of the process[45–47].

Table 5 lists the specific rates of the deuterium–hydrogen exchange defined as the numbers of steps in the H–D exchange adjusted to unit concentrations of the catalyst and the corresponding hydrocarbon, i.e.

$$\nu_{sp} = \frac{\sum i d_i}{[Cp_2V]\,[RH]\,\tau},$$

where $\Sigma i d_i$ is the number of steps in the deuterium–hydrogen exchange in the given hydrocarbon, $[Cp_2V]$ the amount of the catalyst in moles, [RH] the molar concentration of the hydrocarbon, and τ the experimental time (h).

It is of interest that, in the presence of vanadocene under the conditions of the experiments presented in Table 5, the specific rates of the deuterium–hydrogen exchange between methane and benzene, on the one hand, and the deuteroethylene, on the other, are almost equal and in certain cases ν_{sp} for methane is actually higher (Table 6). The anomalously high reactivity of methane compared with benzene is evidently due to the specific features of the mechanism of the activation of the C–H bond in these hydrocarbons by vanadocene.

The cyclopentadienyl rings of the catalyst also participate in the H–D exchange reactions. Table 4 shows that methane is hardly involved in this exchange, while benzene exchanges with the cyclopentadienyl groups only in the absence of ethylene.

The H–D exchange between benzene and C_5D_5 rings results in the formation mainly of hexadeuterobenzene and small amounts of C_6H_5. When ethylene is present in the system, the isotope exchange between benzene and C_5D_5 rings is fully inhibited and there is exchange between the latter and ethylene, which results in the formation of mainly $C_2H_2D_2$. Although the factor associated with the multiple exchange of methylene and benzene with the C_5D_5 rings separately is fairly large, the contribution of this exchange is insignificant in both cases. This is also indicated by the observed satisfactory deuterium atom balance in the exchange between the hydrocarbons investigated in the presence of "light" Cp_2V.[47]

The principal experiment data indicating the multiple character of the H–D exchange between benzene and deuteroethylene in the presence of vanadocene with the preferential formation of C_6D_6 and C_2H_4 show that the coordination of the benzene and ethylene molecules in these intermediate complexes ensures the equivalence of the C–H bonds. The residence time of the benzene and ethylene molecules in the intermediate complexes should then be sufficient for the exchange of all the hydrogen atoms. For example, the complex $(\eta^5\text{-}C_5H_5)_2(\eta^6\text{-}C_6H_6)(\eta^2\text{-}C_2H_4)V$, which has the required symmetrical coordination of benzene and ethylene molecules, can be considered as the intermediate; however, its existence is doubtful for both steric and electronic reasons, because 23 electrons should be present in the transition metal orbitals.

The electronic structue of the complex Cp_2V has been considered[47] for different angles θ between the directions of the V–Cp bonds. Fig. 2 illustrates schematically the positions of the d levels of Cp_2V for different values of θ found by calculations based on the extended Hückel method[50,51].

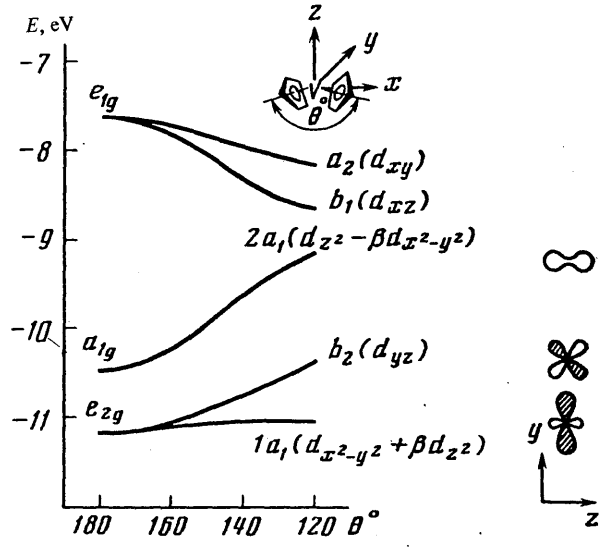
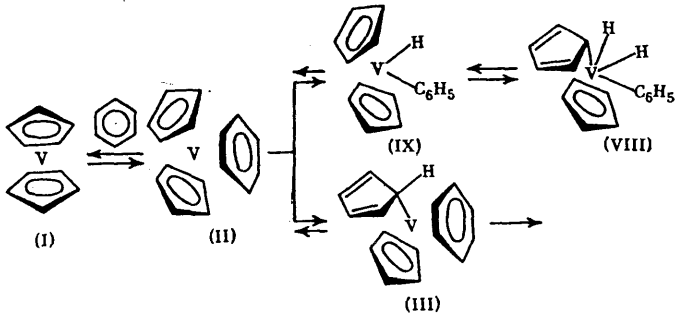
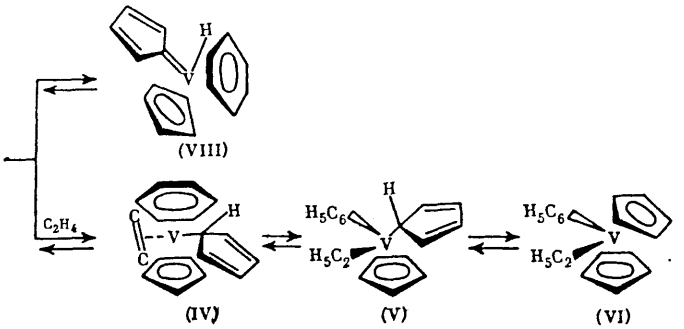


Figure 2. Schematic illustration of the variation of the energy of the d levels in the complex Cp_2V as a function of the variation of the angle θ between the axes of the Cp rings[47].

The distorted Cp_2V complex has three low lying weakly antibonding orbitals: $1a_1$, b_2, and $2a_1$,[47,51,52] which are responsible for the formation of bonds between Cp_2V and ligands of the σ or π type. The sterically accessible electron density maxima in all three orbitals are located in the zy plane. The $1a_1$, b_2, and $2a_1$ orbitals can then ensure the formation of a σ-bond at angles of ±90°, ±45°, and 0° relative to the z axis respectively. The b_2 and $1a_1$ orbitals are suitable for the π interaction at angles of 0°, ±90°, and ±45° relative to the z axis respectively.

The following scheme has been proposed to interpret the main experimental facts observed in the study of deuterium exchange between benzene, on the one hand, and ethylene and Cp rings, on the other[47]:





The first stage is the addition of benzene to Cp_2V; the possibility of complex formation is ensured by the interaction of $2a_1$ and b_2 orbitals of Cp_2V with the orbitals of a_{2u} and e_{1g} of benzene respectively (Fig. 3). The overall energy gain is not very great, since it is made up of the decrease of the energies of two orbitals occupied by four electrons and the increase of the level of one one-electron orbital. Furthermore, there exists also definite steric hindrance to the accommodation of three rings around the vanadium atom.

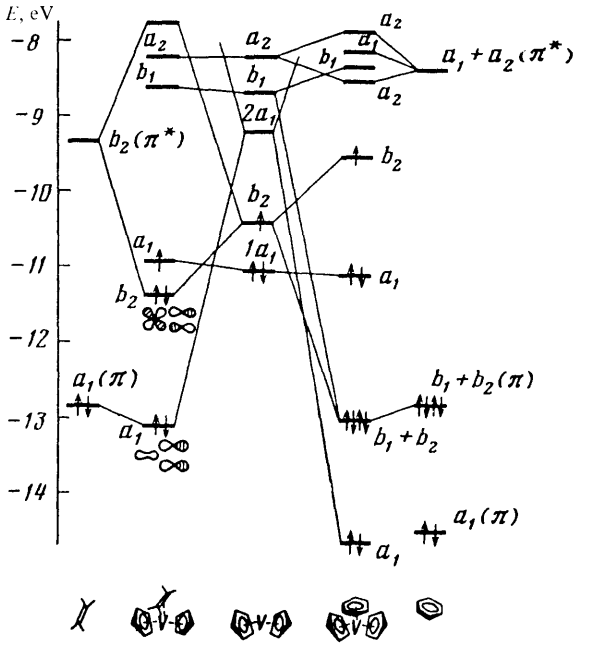


Figure 3. Energy scheme for the interaction of the complex Cp_2V with ethylene and benzene molecules[47].

The presence of a *d* electron in the complex (II) in a high antibonding orbital renders it unstable and reactive, in particular, it tends to be oxidised. The easiest way of employing the reactivity of the complex (II) and of removing an electron from the antibonding *d* orbital consists in attack by the positively charged vanadium atom on the negatively charged rings with formation of the complex (III) or (IX). Attack on the cyclopentadienyl ring is preferred both from the standpoint of the larger negative charge an in view of the possibility of a smooth conversion of η^5-Cp into η^1-Cp via η^3-Cp; this reaction pathway is simplified because there is no need for the dissociation of a C–H bond.

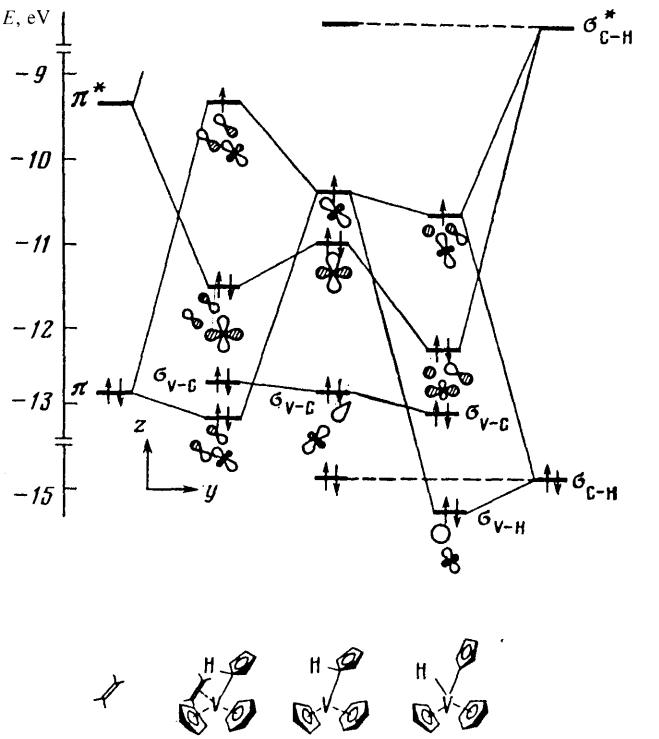
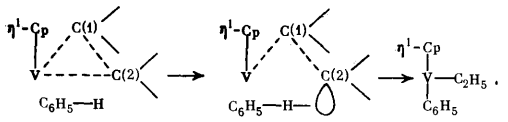


Figure 4. Energy scheme for the interaction of the complex $(\eta^1\text{-Cp})(\eta^5\text{-Cp})(\eta^6\text{-}C_6H_6)V$ with an ethylene molecule and the rearrangement of the orbitals of the complex when a hydrogen atom migrates from η^1-Cp to the vanadium atom[47].

The corresponding low lying orbitals are used for the formation of the $V-\eta^1$-Cp or V–H and $V-C_6H_5$ σ-bonds in the final products of the rearrangement—the complexes (III) and (IX) (Fig. 2). The remaining electrons (three or one) are accommodated in orbitals not involved in interactions with the ligands and for this reason there is no destabilising contribution to the energy in the complex (III) and (IX), in contrast to the initial complex (II). The complex (IX) is apparently thermodynamically somewhat more stable than the complex (III); the latter has orbitals ensuring the σ- and π-binding of C_2H_4 as a result of its interaction with the π and π* orbitals (Fig. 4).[47] A symmetrical coordination of benzene and ethylene obtains in the complex (IV) formed (provided that their rotation in the coordination sphere of the vanadium atom is unhindered). According to calculations by the extended Hückel method, the carbon atoms in the coordinated C_2H_4 molecule are not equivalent. This non-equivalence of the C(1) and C(2) atoms should lead to a difference between the bond lengths, i.e. $l_{V-C(1)} > l_{V-C(2)}$, which facilitates the abstraction of a hydrogen atom from the benzene ring in

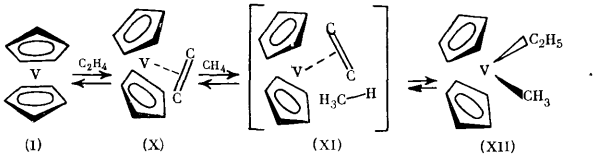
accordance with the scheme[47]



This mechanism agrees with the observed considerable kinetic isotope effect. The complex (V) formed can apparently be converted into the more stable complex (VI) via the shift η^1-Cp → η^3-Cp → η^5-Cp. The reverse transition (VI) → (V) is favoured by the steric hindrance due to the fairly large C_2H_5 and C_6H_5 ligands. The ease of rotation of the fragment η^6-C_6H_6 in the complex (IV) is fairly evident. The possibility of the rotation of the C_2H_4 fragment in the complex $Cp_2V.C_2H_4$ about the V–C_2H_4 axis is due to the electronic factor, since rotation by an angle of 90° results in the disappearance of the stabilising interaction of the b_2 orbital of the vanadium atom with the π* orbital of ethylene (Fig.2). In the complex (IV) there is no symmetry plane owing to the non-equivalence of the five- and six-membered rings and the b_1 and b_2 states are therefore partly mixed. This ensures some stabilisation of the occupied level on rotation of the ethylene molecule by 90° and thereby a decrease of the barrier to the rotation. The results of a semiempirical quantum-mechanical calculation thus confirm a significant decrease of the barrier to rotation.

The occurrence of deuterium exchange between benzene and the C_5D_5 rings, also with the preferential formation of C_6D_6, can be accounted for within the framework of the proposed scheme by the conversion of the complex (III) into the carbene complex (VII).[47]

The difference between the characters of the deuterium–hydrogen exchange reactions of benzene (multiple exchange) and methane (simple exchange) with ethylene supports the view that the proceeds in parallel reactions via different mechanisms. In the case of methane the following scheme appears the most natural:



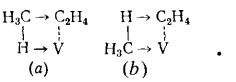
(I) (X) (XI) (XII)

The complex (X) should be fairly stable because Cp_2V has orbitals suitable for the effective π and σ binding of the ethylene molecule (Fig.3). It is evident from the above scheme that, on passing from CH_4 to CD_4, a considerable kinetic isotope effect should be observed.

The sequence of the C_2H_4 and CH_4 addition steps illustrated in the scheme follows from the sharp difference between the coordination properties of these molecules and the instability of the allyl hydride sandwich complexes[48]. In the transition (X) → (XI) → (XII) the cleavage of the double bond in the ethylene molecule facilitates additionally the loosening of the stable C–H bond in methane.

The replacement of methane by benzene immediately precludes the (X) → (XI) stage owing to the steric hindrance, since in the presence of the C···H–C_6H_5 and V···C_6H_5 interactions the ethylene and benzene molecules occupy such a considerable proportion of the space around the vanadium atom that either benzene or ethylene must fall within the region of the van der Waals contact between the Cp rings, which is impossible without a significant increase of the Cp–V bond length and hence without an appreciable energy expenditure[47].

Two possible versions of the addition of the methane molecule can be postulated in the intermediate complex (XI) in conformity with thermodynamics (for the direct abstraction of a hydrogen atom from a CH_4 molecule by the vanadium complex):



(a) (b)

Higher aliphatic hydrocarbons (C_3, C_4, etc.) could not be detected by chromatographic and mass-spectrometric methods in the $Cp_2V + CH_4 + C_2H_4 + C_6H_6$ reaction products. This finding shows that the addition of type (b), in which the interaction between the vanadium atom and a carbon atom is significant, is preferred. The methane molecule should apparently be subjected to preliminary thermal activation and should be made to assume an excited conformation with a partial increase of the H–C–H angle due to deformation vibration. A donor orbital is then formed along the second-order axis of the distorted CH_4 molecule, which determines the interaction with the electropositive vanadium atom.

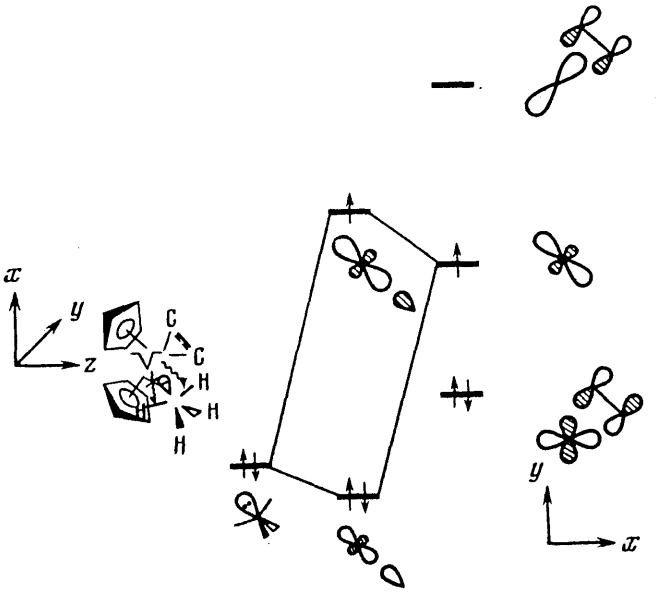


Figure 5. The interaction of the orbitals of a conformationally excited methane molecule with the complex $Cp_2V.C_2H_4$.[47]

The formation of the C_2H_4–CH_3 bond is possible only when the vanadium atom attacks a C–H bond remote from ethylene. However, Fig.5 shows that the presence of a hydrogen atom between the carbon atoms of methane and ethylene gives rise to steric hindrance. When the methyl group is bound to the vanadium atom, this hindrance eliminated, since an H atom from CH_4 naturally adds to C_2H_4. The rotation of the methane molecule about the V–CH axis, which could, in principle, ensure conditions for the formation of a propyl hydride derivative, is energetically unfavourable owing to the considerable increase of the repulsion of methane from the Cp rings and the lack of suitable orbitals for the formation of

the V–H bonds outside the bisector plane. The absence of the above obstacles favours the addition of methane to ethylene, which is apparently characteristic of the $Ti(OR)_4$–AlR_3 system, where the formation of propane from methane and ethylene has been observed[53].

It is natural to expect that ethylene remains in the coordination sphere of the vanadium atom longer than methane. Therefore, and also in view of the asymmetry of the addition of methane relative to ethylene, only mono- and di-deuteromethanes should be observed in the deuterium exchange products, which is consistent with experimental data[45–47] (Table 6).

Comparison of the mechanism of the parallel deuterium–hydrogen exchange reactions between methane and ethylene and between benzene and ethylene shows that the formation of an active centre in the case of benzene requires a longer expenditure of energy. This is in fact the reason for the observed high reactivity of methane compared with benzene in the exchange reaction of ethylene. The hindrance of the H–D exchange following the replacement of methane by heavier alkanes is also to be expected from these ideas.

It follows from the data presented above for the mechanism of the oxidative addition of methane that a decrease of the catalytic activity should be observed in the series of 3*d* transition metal metallocenes with enhancement of the electron-donating properties of the metal atom. The results of a study of the H–D exchange between deuteroethylene and methane and benzene in the presence of different metallocenes (Table 6) show that a sharp decrease of the rate of the H–D exchange involving methane is observed with enhancement of the electron-donating properties of the 3*d* transition metal atom in the sequence Ti > V > Mn > Fe > Co > Ni, while the multiple exchange factor changes insignificantly.

These results confirm yet again that the isotope exchange between methane and ethylene takes place as a result of the oxidative addition of methane to the transition metal complex of ethylene, i.e. as a result of the reaction which is the opposite of the disproportionation of the alkyl groups bound to the metal atom.

IV. THE "ALKANOLYSIS" OF THE TRANSITION METAL–CARBON BOND

The studies by Enikolopov and co-workers of the activation of methane by organometallic Ziegler–Natta catalysts demonstrated for the first time that, by analogy with hydrogen, methane can also participate in the dissociation of the transition metal–carbon σ-bond[34,53].

As mentioned above, the hydrogenolysis of the M–C bond plays an important role in the hydrogenation reactions of unsaturated hydrocarbons[38] and in the processes involving the regulation of the molecular weight of polyolefins during their synthesis in the presence of Ziegler–Natta catalysts[54]. In this case the reaction leads to the formation of the corresponding alkane and a metal–hydride linkage.

The reaction of methane with the M–C σ-bond leads to the formation of a methyl derivative of the transition metal and an alkane molecule:

$$\rangle M{-}R + CH_4 \rightarrow \rangle M{-}CH_3 + RH \quad .$$

By analogy with hydrolysis, hydrogenolysis, alcoholysis, etc., this reaction can be called "alkanolysis" (although for other alkanes a reaction of this type has not so far been observed) or the hydromethylation of the M–C bond.

"Alkanolysis" is observed in various catalytic systems based on $TiCl_4$, Cp_2TiCl_2, VCl_4, $V(acac)_3$, $Fe(acac)_3$, and many other transition metal derivatives in combination with various organoaluminium compounds. The rate of the process depends on the nature of the transition metal, the length of the hydrocarbon group bound to it, and other factors.

The most convincing demonstration of the occurrence of "alkanolysis" was achieved in the study of the interaction of methane, carefully freed from traces of moisture and oxygen, with catalytic systems. It is known[3] that in the interaction of the components of Ziegler–Natta systems containing triethylaluminium or diethylaluminium chloride the evolution of ethane and ethylene is observed, the amount of the latter being much smaller than that of ethane. Fig. 6 presents as an example data for the kinetics of the evolution of ethane in the $Fe(acac)_3$–$Al(C_2H_5)_3$ catalytic system[53].

Fig. 6 shows that ethane is evolved in an amount almost equivalent to the initial iron content over a period 5–10 min in the absence of methane; subsequently the evolution of ethane ceases. In the presence of methane the "alkanolysis" of the Fe–C_2H_5 σ-bond results in the evolution of a much larger amount of ethane. Trideuteromethane (CD_3H/Fe = $2{,}2 \times 10^{-4}$) is detected in the products of the hydrolysis of the catalytic system treated with tetradeuteromethane, which indicates the formation of a methyl derivative of iron in the "alkanolysis" of the Fe–C_2H_5 bond. According to preliminary data, the rate constants for the "alkanolysis" of the M–R bond are smaller by a factor of 30–50 than the rate constants for the hydrogenolysis of the same bond. "Alkanolysis" is a reaction which can already find an important practical application, for example, in the manufacture of polyolefins.

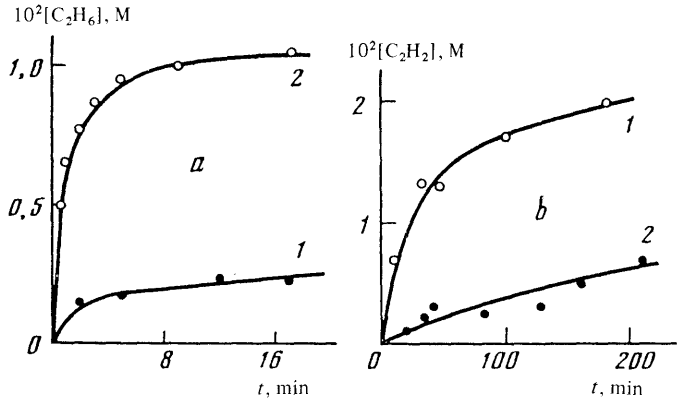


Figure 6. Kinetics of the accumulation of ethane (*a*) and of the absorption of acetylene (*b*) in the $Fe(acac)_3$–$Al(C_2H_5)_3$ catalytic system in the absence (curves *1*) and presence (curves *2*) of methane[53].

V. THE ADDITION OF METHANE TO UNSATURATED HYDROCARBONS

The discovery of the deuterium–hydrogen exchange reaction involving methane and of the "alkanolysis" of the M–C bond, which proceeds analogously to the corresponding reactions of hydrogen with organometallic catalysts, led to the task of finding new ways for the transformation of methane.

The most characteristic and important reaction of hydrogen in the presence of Ziegler–Natta catalysts is hydrogenation of unsaturated hydrocarbons. The mechanism of the hydrogenation reaction involves stages in which the transition metal–carbon bond undergoes hydrogenolysis and a hydrocarbon molecule is inserted in the metal–hydride bond formed[38]. For example, the mechanism of the hydrogenation of ethylene can be represented schematically as follows:

$$\rangle M{-}R + H_2 \rightarrow \rangle M{-}H + RH\ ,$$
$$\rangle M{-}H + C_2H_4 \rightarrow \rangle M{-}C_2H_5 + H_2\ ,$$
$$\rangle M{-}C_2H_5 + H_2 \rightarrow \rangle M{-}H + C_2H_6\ .$$

The discovery of "alkanolysis" led to the idea that hydrogen may be replaced by methane in the hydrogenation reactions of ethylene and acetylene[53 55]. Indeed, the "alkanolysis" of the M–R σ-bond in the catalytically active complex results in the formation of a new $M{-}CH_3$ σ-bond. It is known[33] that the insertion of an ethylene molecule in the bond results in the formation of a propyl derivative of the transition metal:

$$\rangle M{-}CH_3 + C_2H_4 \rightarrow \rangle M{-}C_3H_7\ .$$

This reaction is much faster than the insertion of ethylene in an M–H bond[53]. The "alkanolysis" of the $M{-}C_3H_7$ bond obtained should result in the formation of a propane molecule—the product of the addition of methane to ethylene:

$$CH_4 + C_2H_4 \rightarrow C_3H_8\ .$$

The possibility, in principle, of the occurence of this reaction was first demonstrated in the presence of the $Ti(C_4H_9O)_4{-}Al(C_2H_5)_3$ catalytic system in benzene at 20 °C and a pressure of 1 atm.[55] Under these conditions, in the absence of methane, ethylene dimerises with formation of but-1-ene. The subsequent addition of the monomer, leading to the growth of the polymer chain, is hardly observed in this system[57].

If the catalytic system is maintained in an atmosphere of ethane in the absence of ethylene, then ethane, the product of the "alkanolysis" of the $Ti{-}C_2H_5$ bond, accumulated in the gas phase[55,58]. As a result of this reaction, a small amount of the methyl complex of titanium is formed in the system. After the supply of ethylene to the system in proportions $CH_4/C_2H_4 > 10$, its absorption with formation of propane is observed. This is accompanied by the simultaneous formation of a small amount of but-1-ene, whose yield can be reduced by increasing the molar ratio of methane and ethylene or by altering the conditions in the treatment of the catalyst with methane. Under the conditions indicated, the yield of propane after 10 h is 15–20% of the amount of ethylene in solution. It is noteworthy that the efficiency of the catalyst is not high and that approximately 1 mole of propane is formed in the presence of 4–5 moles of the initial titanium[55].

The formation of propane is not observed in the absence of methane or ethylene. When methane is replaced by deuteromethane, tetradeuteropropane $C_3H_4D_4$ is detected mass-spectrometrically in the gaseous products[55]. Thus there is no doubt about the formation of propene from methane and ethylene.

In order to achieve the addition of methane to acetylene, i.e.

$$CH_4 + C_2H_2 \rightarrow CH_3{-}CH{=}CH_2\ ,$$

studies were made of various catalysts of the hydrogenation of acetylene based on titanium(IV), iron(III), cobalt(II), and nickel(II) complexes in combination with organoaluminium compounds[53]. Among these, catalytic activity in the reaction involving the addition of methane to acetylene was shown only by the $Fe(acac)_3{-}Al(C_2H_5)_3$ system in benzene solution. It is known from the literature[59] that acetylene polymerises in the presence of this catalyst. However, after the treatment of the catalytic system with carefully purified methane, the polymerisation of acetylene is not observed and the rate of its absorption falls significantly[53] (Fig. 6b).

Thus, by interacting with the active centres of the catalyst, methane converts them into a form inactive for polymerisation. Bearing in mind that ethane is evolved in this process, the decrease of the catalytic activity can be attributed to the formation of a methyl derivative of the transition metal with a much lower reactivity in the initiation of the polymer chain[33,37]. Evidently the presence of the relatively inactive $M{-}CH_3$ bond in an excess of methane ($CH_4/C_2H_2 \geq 30$) ensures the necessary condition for the single insertion of an acetylene molecule in this bond and the formation of propene in the system[53].

In a dilute solution of the catalyst propene accumulates after an appreciable induction period whose duration depends on the catalyst concentration. Table 7 shows that the yield of propene increases with time and with temperature. With increase of the molar ratio Al/Fe, the yield of propene falls and, when Al/Fe > 8, whereupon the rate of exchange of the alkyl groups bound to the iron and the aluminium atoms increases significantly, its formation is not observed and acetylene polymerises[53].

Table 7. The yields of propene Q in the reaction of methane and acetylene under the influence of the $Fe(acac)_3{-}Al(C_2H_5)_3$ catalytic system[53]*.

10^3[Fe(acac)$_3$], M	T, °C	t, min	$10^2 Q$, mol/mol Fe	10^3[Fe(acac)$_3$], M	T, °C	t, min	$10^2 Q$, mol/mol Fe
1	14	240	1.6	1	30	51	1.6
1	20	100	—	10	20	40	0.5
1	20	135	0.4	10	20	70	0.8
1	20	255	1.0	10	20	95	0.9
1	20	280	2.8	10	20	240	1.0

*Solvent—benzene; pressure 640 mmHg; $[CH_4] = 1.93 \times 10^{-2}$ M; $[C_2H_2] = 0.6 \times 10^{-2}$ M; Al/Fe = 4.

In the absence of methane or acetylene, propane is not formed, while the replacement of methane by deuteromethane, results in the detection of deuteropropene in the reaction products. It was noted above that, after the hydrolysis of the catalytic system treated with tetradeuteromethane, trideuteromethane is formed in small amounts ($CD_3H/Fe = 2.2 \times 10^{-4}$).[53] This fact shows that the fraction of the active centres responsible for the addition of methane to acetylene, relative to the total amount of iron in the system, is small. This is evidently the reason for the observed low yield of propene relative to the initial amount of the catalyst.

Enikolopov presented for the first time the results of studies on reactions involving the addition of methane to unsaturated hydrocarbons (ethylene and acetylene) in the 1979 Medvedev lectures. This fundamentally new reaction of paraffinic hydrocarbons aroused much interest not only in our country but also abroad. Studies on the activation of alkanes by non-platinum metal complexes are being vigorously prosecuted in many laboratories at the present time.

The formation of propene in the H_2–CH_4–C_2H_4–C_2H_2 mixture in the presence of a catalytic system based on nickel(II) stearate, naphthenate, and naphthenehydroxamate, deposited on the surface of nickel hydroxide, in combination with triethylaluminium or di-isobutylaluminium hydride has also been reported by Noskova and co-workers[60,61]. In the presence of these catalysts it is possible to obtain propene in higher yields. However, unfortunately, owing to the complexity of the system proposed in these investigations, the role of methane in the formation of the propene molecule has not so far been unambiguously established. The situation is also complicated by the fact that the formation of a small amount of propene in the system is observed also in the absence of methane, apparently as a result of the metathesis of ethylene. Despite this, the above studies merit special attention, since there is no doubt about the activation of methane in these systems.

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Analysis of the literature data on the catalytic activation of alkanes indicates a vigorous development of the chemistry of saturated hydrocarbons. In the presence of 3*d* transition metal complexes, a fundamentally new type of reactions of methane, namely addition reactions, has been discovered. By adding methane to unsaturated hydrocarbons (in particular to acetylene), it is possible to obtain the most important petroleum processing products from a non-petroleum raw material—natural gas. The possibility of the practical application of this process arises owing to the development of highly active catalysts, which make it possible to increase sharply the yield of the product (for example, propene) per unit mass of the catalyst. We believe that, under the conditions of the vigorous development of the research in this field, the practical application of the available results is a matter for the near future.

The possibility, in principle, of achieving the hydromethylation of various compounds with the aid of methane leads to new ways of synthesising various organic compounds using the side products from the processing of petroleum, natural gas, and coal. The range of thermodynamically feasible reactions involving methane is fairly wide. These reactions include, for example, the hydromethylation of allene, leading to the formation of butenes, the formation of ethyl methyl ketone from methane, carbon monoxide, and ethylene (analogously to the hydroformylation reaction), the synthesis of acetaldehyde from methane and carbon monoxide at elevated pressures, and many others. The search for the selective catalysts of these and other most important reactions of alkanes (oxidation, chlorination, dehydrogenation, etc.) is being actively prosecuted in various countries[22–31,40–47,60–70]. One must note that studies of Soviet investigators have played a leading role in the catalytic activation of alkanes; these investigations have already significantly enriched the chemistry of alkanes.

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Branch of the Institute
of Chemical Physics,
USSR Academy of Sciences,
Chernogolovka,
Moscow Region

Russian Chemical Reviews

March 1984

Review articles by scientists at the Nesmeyanov Institute of Organoelemental Compounds of the USSR Academy of Sciences (awarded the Order of Lenin), founded thirty years ago in 1954 from a number of branches of the Zelinskii Institute of Organic Chemistry of the USSR Academy of Sciences on the initiative of the outstanding Soviet chemist Academician A.N.Nesmeyanov, are collected in this issue of the Journal. During the past years, this Institute, which is the first one in the world to deal with the chemistry of organoelemental compounds, grew into a major scientific research establishment and acquired great authority in world science. This authority is due to the fundamental studies by Academicians A.N.Nesmeyanov, K.A.Andrianov, M.I.Kabachnik, I.L.Knunyants, V.V.Korshak, I.V.Obreimov, O.A.Reutov, and A.V.Fokin, as well as the Corresponding Members of the USSR Academy of Sciences M.E.Vol'pin, D.N.Kursanov, and R.Kh.Freidlina.

A.N.Nesmeyanov discovered the phenomenon of metallotropism, investigated the properties of sandwich compounds, and devised new methods for the synthesis of the σ- and π-complexes of transition metals—organometallic chelates. Important discoveries such as those of the rearrangement of radicals in solution with 1,2-migration of chlorine and the fixation of molecular nitrogen by transition metal complexes under mild conditions have been made in the Institute. A new allotropic modification of carbon, namely carbyne, has been discovered, and a new synthetic method, ionic hydrogenation of unsaturated compounds, has been proposed.

The modern chemistry of organic derivatives of phosphorus, fluorine, and silicon, the synthetic chemistry of polymers, and many other branches of chemical science have been developed.

In view of its major services to chemical sciences and in the training of scientific cadres, the Nesmeyanov Institute of Organoelemental Compounds of the USSR Academy of Sciences was awarded the Order of Lenin in 1967.

Translated from *Uspekhi Khimii*, 53, 370-397 (1984) U.D.C. 542.971.2:542.952:655.552

Modern Problems of Homolytic Telomerisation

R.Kh.Freidilina, F.K.Velichko, and A.B.Terent'ev

The results of studies in homolytic telomerisation during the last decade at the Institute of Organoelemental Compounds of the USSR Academy of Sciences are surveyed. The synthetic possibilities which have arisen as a result of initiation by metal carbonyls are demonstrated. The prospects for the practical utilisation of telomerisation are discussed.
The bibliography includes 173 references.

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I. INTRODUCTION

Telomerisation is understood as a radical chain process in which a molecule of any kind of saturated compound (telogen) combines with several molecules of an olefin or another unsaturated compound. Formally, the reaction can be expressed by Eqn.(2) of Scheme 1; it fills the "gap" between addition and polymerisation:

Scheme 1

(1) $X-Y + C=C \longrightarrow X-C-C-Y$ (addition),

(2) $X-Y + n\,C=C \rightarrow X-(C-C)_n-Y$ (telomerisation; $n = 2$-20)

Telomers

(3) $X-Y + n\,C=C \rightarrow X-(C-C)_n-Y$ (polymerisation; $n \rightarrow \infty$).

This comparatively new field began to develop in the postwar years. At the present time systematic and extensive researches into telomerisation are prosecuted in the USSR, the USA, Japan, Italy, the Federal Republic of Germany, and France.

Telomerisation is a typical organic reaction; it makes it possible to synthesise under similar conditions homologous series of polyfunctional compounds of different classes by selecting appropriate telogen–monomer pairs. The studies by Soviet investigators, and in particular by the team at the Institute of Organoelemental Compounds of the USSR Academy of Sciences, have in many respects enriched the theoretical and practical aspects of telomerisation and have led to its transformation from a purely laboratory reaction into a process suitable for technological application[1-3].

Two monographs and a number of reviews[1,4], among which we shall mention only those published in recent years[5-12], have been devoted to telomerisation. The concept of telomerisation has been included in an encyclopaedia[13] and in textbooks of organic chemistry[14]. The rate of development of researches in this field is so great that it has now become necessary to write new reviews and monographs.

New important branches of telomerisation have developed extensively in recent years and its applications in organic synthesis, in the study of general problems of radical chemistry, and in practice have been greatly expanded.

This includes the discovery of fundamentally new initiators and initiating systems which made it possible to involve in telomerisation many new types of telogens and monomers as well as their new combinations which had been previously believed to be ineffective in this process. Instances of telomerisation accompanied by the rearrangement of growing radicals have been extensively studied. Investigations have been developed into stepwise telomerisation and the cotelomerisation of two monomers with one telogen. Practical applications in which telomerisation makes it possible to solve important problems have been found. New methods have been developed for the isolation of telomers as well as schemes for demonstrating their structure by methods of physical organic chemistry. The most important advances achieved in the field of telomerisation during the last decade are considered in this review.

II. GENERAL PROBLEMS OF TELOMERISATION

Monomers. In principle any unsaturated compound capable of radical polymerisation can be used in free-radical telomerisation; ethylene, alk-1-enes, vinyl chloride, vinylidene chloride, perfluoroethylene, chlorofluoroethylenes, allyl and acrylic compounds, and diene hydrocarbons and their derivatives have been studied in greatest detail and are frequently used.

Telogens. Substances containing bonds which readily undergo homolytic dissociation are used as telogens:



The types of such bonds whose dissociation leads to telomerisation are presented below:

C—H	B—H	SO_2—Hal
C—C	N—Hal	Si—H
C—Cl	P—H	Sn—H
C—Br	S—H	Cl—H
C—I	S—Hal	Br—H
	S—S	I—H

Reaction mechanism. The generally accepted mechanism of telomerisation initiated by radical-forming substances is presented in Scheme 2.

Scheme 2

(1) Initiator $\rightarrow$ R$^{\cdot}$
(2) R$^{\cdot}$ + X—Y $\rightarrow$ RX + Y$^{\cdot}$ } (initiation)

(3) Y$^{\cdot}$ + CH_2 = CHR $\rightarrow$ $YCH_2\dot{C}HR$
(4) $YCH_2\dot{C}HR + n CH_2 = CHR \xrightarrow{k_p} Y(CH_2CHR)_nCH_2\dot{C}HR$ } (growth of radical)

(5) $Y(CH_2CHR)_nCH_2\dot{C}HR$ + X—Y $\xrightarrow[\text{telomers}]{k_{tr}}$ $Y(CH_2CHR)_{n+1}X$ + Y$^{\cdot}$ (chain transfer)

(6) Radicals $\rightarrow$ inactive products (chain termination)

Here k_p and k_{tr} are the chain propagation and chain transfer constants respectively and $n = 1,2,3, \ldots$

In most instances the telomerisation reactions initiated by peroxides, azo-compounds, and light proceed in accordance with this scheme in which chain transfer directly to the telogen [stage (5) of scheme 2] takes place. However, many examples of telomerisation in which Scheme 2 does not hold have now accumulated. The importance of Scheme 2 consists in the fact that in many cases of smooth telomerisation under rigorously controlled conditions it is possible, knowing the distribution of the telomers in terms of the number of monomer units to estimate comparatively simply the relative rates of the intermediate stages—for example, the partial chain transfer constants C_n can be determined from the Mayo equation[15]:

$$C_n = k_{tr}/k_p = Q \cdot \left(T_n \Big/ \sum_{n+1}^{\infty} T_i \right) ,$$

where Q is the molar ratio of the monomer and the telogen and T_n the molar yield of the telomer incorporating n monomer units. A characteristic feature of the partial constants C_n, in contrast to the general chain transfer constants C_∞ determined from radical polymerisation data, consists in the fact that they reflect the influence of the fragment Y of the telogen on the radical centre in the telomer-radicals $Y(CH_2CHR)_n^{\cdot}$. For many telomerisation processes, the constants C_n increase as n increases from 1 to 4–5 (Table 1) and only then assume constant values. They make it possible to estimate the reactivities of the intermediate radicals, telogens, and monomers.

Initiation. The independence of C_n on the nature of the radical-forming compound and, within certain limits, of its concentration (at the same temperature) shows that the initiator is not involved in the chain propagation and transfer stages. The initiation of telomerisation by radical-forming substances such as acyl and alkyl peroxides, azo-compounds, and similar compounds is restricted to a fairly narrow class, since the reaction proceeds only with telogens containing an *E–E'* bond readily susceptible to homolytic dissociation. For example, peroxides and azobisisobutyronitrile successfully initiate the telomerisation of olefins with CCl_4 but are incapable of initiating the analogous reactions involving the C–Cl bond with compounds of the type RCH_2CCl_3.[9] On the other hand, the major influence of polar affects on the course of telomerisation has been discovered. When the polar effects of the telogen and the monomer are of the same kind, even extremely reactive compounds do not react via the telomerisation mechanism under the conditions of the method of initiation indicated. Thus, on initiation with peroxides, azo-compounds, or ultraviolet light, acrylic monomers are not telomerised by the esters of α-bromo-substituted acids, chloroform, and carbon tetrachloride[10]; instead of undergoing telomerisation, the monomer polymerises. Nevertheless, these initiation methods retain fully their importance for telomerisation, particularly telomerisation involving the dissociation of a C–H bond.

A new important procedure involves the use of metal carbonyls for the initiation of telomerisation. Carbonyls were employed for this purpose for the first time in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Synthesis of the USSR Academy of Sciences in 1959–1961.[13] As will be shown below, when halogen-containing telogens are used, the initiation of the telomerisation by mononuclear metal carbonyls can be described by Scheme 3:

Scheme 3

$$M(CO)_n \rightleftarrows M(CO)_{n-1} + CO ;$$

$$\rangle C—Hal + M(CO)_{n-1} \rightarrow \rangle C^{\cdot} + HalM(CO)_{n-1} .$$

(A)

Next the reaction proceeds via stages (3)–(6) of Scheme 2 (Y = $\rangle C^{\cdot}$) or, in contrast to the initiation of the telomerisation by radical-forming substances, the intermediate metal carbonyl halide (A) participates in the chain transfer stage, transferring the halogen to the growing radical via Scheme 4 (where $m = 0,1$):

Scheme 4

$$(A) + Y(CH_2CHR)_m CH_2\dot{C}HR \rightarrow Y(CH_2CHR)_{m+1}Hal + M(CO)_{n-1} .$$

The metal-containing species $M(CO)_{n-1}$ arising in this stage participates in the transfer of the kinetic chain, abstracting the halogen from the telogen, as shown in Scheme 3.

This is a very flexible initiation procedure, since, by varying the nature of the metal carbonyl, it is possible to achieve reactions which proceed with very great difficulty. It has now been found that the complexes of metal carbonyls with various ligands, i.e. $M(CO)_{n-1}L$, as well as the combination of the metal carbonyl and the ligand taken separately, i.e. $M(CO)_n$ + L are even more active telomerisation initiators. Subsequently, both in the studies in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Synthesis of the USSR Academy of Sciences and in the studies by foreign investigators, a wide range of initiating systems were applied, including various transition metal compounds (carbonyls, halides, chelates, and π-complexes) in combination with various activating additives (co-initiators)—alcohols, amines, amine hydrochlorides, nitriles, carboxylic acid esters, phosphorous acid esters, dimethylformamide (DMF), etc.[13]

Chain transfer. A wide variety of forms of chain transfer in telomerisation have now been discovered. Apart from the reactions with chain transfer by the growing radicals to the telogen [stage (5) of Scheme (2)]. reactions have been found in which chain transfer proceeds via the fragmentation of the growing radical (Scheme 5), via the oxidation of the growing radical (Scheme 6), and via the transfer of the halogen from metal carbonyl halides (Scheme 4). For example, for the telomerisation of ethylene by tetrachloroethylene (initiator—t-butyl peroxide (TBP)], we suggested[16] that chain transfer takes place via the fragmentation of the growing radical in accordance with Scheme 5:

Scheme 5

$$CCl_2{=}CCl_2 + n CH_2{=}CH_2 \xrightarrow{TBP} Cl(CH_2CH_2)_nCCl{=}CCl_2 ;$$

(1) (TBP) $\rightarrow$ 2R$^{\cdot}$;

(2) R$^{\cdot}$ + $CCl_2{=}CCl_2 \rightarrow RCCl_2\dot{C}Cl_2 \rightarrow RCCl{=}CCl_2 + Cl^{\cdot}$;

(3) Cl$^{\cdot}$ + n $CH_2{=}CH_2 \rightarrow Cl(CH_2CH_2)_n^{\cdot}$;

(4) $Cl(CH_2CH_2)_n^{\cdot} + CCl_2{=}CCl_2 \rightarrow Cl(CH_2CH_2)_n CCl_2\dot{C}Cl_2$ (B) ;

(5) $Cl(CH_2CH_2)_nCCl_2\dot{C}Cl_2 \xrightarrow{\text{fragmentation}} Cl(CH_2CH_2)_nCCl{=}CCl_2 + Cl^{\cdot}$.

There is no doubt that the chain transfer by the radical (B) to the telogen does not occur both as a consequence of the low reactivity and considerable stability of this radical and owing to the low probability of the abstraction of a chlorine atom from tetrachloroethylene. The radicals (B) undergo fragmentation with formation of the final products and the elimination of the chain propagating chlorine atom. Such telomerisation is accompanied by the formation of a number of side products; in particular, extensive chlorination takes place with evolution of hydrogen chloride, which is also consistent with the hypothesis of the intermediate formation of atomic chlorine.

A new type of telomerisation, in which there is undoubtedly no usual chain transfer to the telogen, has been found[17-21]; it was shown that contrary to the literature data, under the conditions of the Meerwein reaction it is possible to achieve the telomerisation of ethylene, acrylonitrile, and vinylidene chloride by arenediazonium chlorides (Scheme 6):

Scheme 6

$$ArN_2Cl + nCH_2=CHX \xrightarrow[CH_3COONa]{CuCl_2/CuCl} Ar(CH_2CHX)_nCl + N_2 ;$$

(1) $ArN_2Cl \xrightarrow{CuCl} Ar^{\cdot}$;

(2) $Ar^{\cdot} + CH_2=CHX \rightarrow ArCH_2\dot{C}HX$;

(3) $ArCH_2\dot{C}HX + nCH_2=CHX \rightarrow Ar(CH_2CHX)_n^{\cdot}$;

(4) $Ar(CH_2CHX)_n^{\cdot} + ArN_2Cl \not\rightarrow$ (do not react);

(5) $Ar(CH_2CHX)_n^{\cdot} + CuCl_2 \rightarrow Ar(CH_2CHX)_nCl + CuCl$;

$Ar = C_6H_5$, n-$NO_2C_6H_4$, o-$CH_3C_6H_4$; X = H, CN, $COOCH_3$; $n = 1, 2$.

All the stages of this reaction, except stage (3), had been proposed earlier. We were able to obtain telomers and demonstrate thereby that stage (3) can take place[21]. In this case direct chain transfer via stage (4) is undoubtedly ruled out; the growing radical is stabilised in the oxidation-reduction reaction with $CuCl_2$ via stage (5).

Certain examples in which the telomerisation does not obey the usual mechanism with chain transfer to the telogen were enumerated above. However, the reactions of the usual type (Scheme 2) have been most thoroughly investigated, including investigations by kinetic methods.

Chain termination is the least investigated stage in the telomerisation mechanism. It has been frequently suggested that chain termination takes place as a result of the dimerisation or disproportionation of radicals. However, tests in relation to the telomerisation of cyclohexene, heptene, and propene by trifluoroiodomethane[22] and carbon tetrachloride[23] did not confirm this hypothesis. In the case of carbon tetrachloride[23] the formation of hexachloroethane was not observed, but the hydrides of the intermediate radicals, obtained as a result of the "allyl termination", were found. Instances (for example, in the telomerisation of isobutene by aliphatic acids[24]) where the recombination and cross-recombination reactions of radicals play a significant role and the yield of the corresponding compound is comparable to that of the telomers have been discovered in recent years.

Thus a wide variety of reactions with different types of initiation and chain transfer and termination mechanisms, depending on the structure of the telogen and the monomer and also on the nature of the initiating system, can be achieved at the present time by the telomerisation method. This has greatly extended the scope of the utilisation of telomerisation for synthetic purposes.

III. METAL CARBONYLS AS INITIATORS OF A NEW TYPE

Interesting features have been discovered in telomerisation using initiators of a new type—variable valence compounds and carbonyls of Group VI–VIII metals. Freidlina and Belyavskii showed in 1959[25,26] that iron, chromium, molybdenum, and tungsten carbonyls effectively initiate the homolytic telomerisation of ethylene with CCl_4, $CHCl_3$, and CCl_3COOR. Since then initiating systems based on transition metal carbonyls have been widely used in homolytic chain reactions involving both telomerisation[9,10,12,27] and polymerisation[28,29]. The data accumulated suggest that in this case we are dealing with a new branch of homogeneous catalysis—the metal carbonyl-initiated homolytic chain reactions. The study of the application of redox initiators (the character of the initiating action of which resembles in many respects that of metal carbonyls), mainly iron and copper halides and complex cyanides[30-32] as well as chlorine-containing iron complexes of the type $[L_4Fe^{III}Cl_2]_2[Fe^{II}Cl_4]$, where L = DMF or dimethyl sulphoxide (DMSO), and $[(CH_3CN)_6Fe^{II}][Fe^{III}Cl_4]_2$ in telomerisation was prosecuted simultaneously[33]. Both these large groups of metal-containing initiators are combined[12] in the broad concept of coordination initiators, whose application significantly expands the synthetic scope of telomerisation, namely (1) it makes it possible to regulate the composition of the telomerisation mixture, driving the telomerisation reaction towards the formation of lower telomers up to 70–80% yield of the adduct relative to the sum of the telomers, (2) it directs telomerisation selectively to the C–Hal bond in the presence of reactive C–H and C–Hal bonds in the telogen, (3) it makes it possible to introduce into the telomerisation reaction telogens with the trichloromethyl group which is inert under the conditions of peroxide initiation, (4) it permits the telomerisation of readily polymerisable monomers such as acrylic compounds, styrene, and vinyl chloride, (5) it leads to a simple way of synthesising branched telomers in accordance with a stepwise telomerisation scheme (see Section VI), and (6) it increases the selectivity of the photoinitiation driving the reaction towards the rupture of the C–Hal bond.

Metal carbonyls are the most promising initiators. Differing appreciably (depending on the metal) in their activity in the initiation stage and in their ability to participate in the chain transfer stage, suitably selected metal carbonyls make it possible to achieve any of the synthetic possibilities in telomerisation enumerated above or to obtain a combined result.

In terms of their interaction with the telogen, the monomer, the co-initiator, and finally the growing radical, metal carbonyls effective in telomerisation can be divided into three groups. The first group includes carbonyls capable of abstracting a halogen atom from the telogen in the initiation stage and of transferring it to the growing telomer radical, regenerating at the same time the halogen abstracting species. In other words, these carbonyls are capable of participating in the chain transfer stage without interrupting the kinetic chain. This group includes $Fe(CO)_5$ and its derivatives with the ligand L in the coordination sphere of iron $[L_nFe(CO)_{5-n}]$.

The second group comprises carbonyls capable of abstracting a halogen atom from the telogen in the initiation stage but incapable of transferring it to the growing telomer radical. It includes chromium, molybdenum, and tungsten hexacarbonyls.

The third group is made up of dinuclear carbonyls with a metal–metal bond, for the initiating capacity of which the conditions in the homolytic dissociation of the metal–metal

bond are of decisive importance; their interrelations with the components of the reaction mixture are frequently manifested in an extremely complex manner. This group includes $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, and $[Cp_2Fe(CO)_2]_2$, as well as, apparently, $[CpW(CO)_3]_2$ and $[CpMo(CO)_3]_2$, which are capable of forming metal-centred radicals[34].

The addition of chloroform to alk-1-enes can serve as a test reaction for the classification of metal carbonyls[35-38]. Chloroform is able to react with dissociation of both C–Cl and C–H bonds in different sequences depending on the character of the initiation (Scheme 7).

Scheme 7

(1) $CCl_3{-}H \rightarrow \dot{C}Cl_3 \xrightarrow{-C=C-} CCl_3\dot{C}{-}\dot{C}- \xrightarrow{CCl_3-H} CCl_3C{-}\dot{C}H$;

(2) $Cl\,CH{-}Cl \rightarrow \dot{C}HCl_2 \xrightarrow{-C=C-} CHCl_2\dot{C}{-}\dot{C}- \xrightarrow{CCl_3-H} CHCl_2C{-}\dot{C}H$;

(3) $Cl_2CH{-}Cl \rightarrow \dot{C}HCl_2 \xrightarrow{-C=C-} CHCl_2\dot{C}{-}\dot{C}- \xrightarrow{CHCl_2-Cl} CHCl_2C{-}CCl$.

Eqn.(1) represents the peroxide type of initiation: the C–H bond is dissociated in the initiation and chain transfer stages and the initiator is not involved in the chain transfer stage. Eqn.(2) represents a mixed type of initiation: the metal carbonyl participates in initiation but not in chain transfer; the initiation involves the C–Cl bond and the chain transfer involves the C–H bond. Eqn.(3) represents metal carbonyl initiation where the carbonyl participates in the initiation and chain transfer stages; the initiation and chain transfer take place with dissociation of the C–Cl bond.

In the case of iron pentacarbonyl, which, depending on the conditions, can either react directly via reactions of types (2) and (3) of Scheme 7 or indirectly via a reaction of type (1) (forming a radical $R^{\cdot}$ capable of abstracting a hydrogen atom from chloroform), in each specific reaction it is necessary to take into account the tendency of $Fe(CO)_5$ to form complexes with the monomer[39] and the co-initiator[40-42]. In the case of a weakly polar monomer exhibiting a small capacity for complex formation with iron carbonyl (for example, ethylene), the metal carbonyl is not involved in the chain transfer stage when $Fe(CO)_5$ is used in small amounts (< 5 mole %) without an initiator and the distribution of the telomer homologues in the telomerisation of CCl_4 or $CHCl_3$ with C_2H_4 does not differ from their distribution in peroxide initiation[26,27].

It has been shown for monomers forming comparatively stable complexes with $Fe(CO)_5$ (propene and specially vinyl chloride) in relation to telomerisation with CCl_4 and $CHCl_3$ [39,40] that, at a low $Fe(CO)_5$ concentration and for a long kinetic chain, only the initiating activity of the carbonyl is manifested in the reaction, i.e. it is able to generate $\dot{C}Cl_3$ radicals and the chain transfer constants do not differ from those in the peroxide initiation. With increase of the $Fe(CO)_5$ concentration, the content of the adduct in the mixture of telomers increases appreciably and C_1 can be significantly greater than in the peroxide initiation, i.e. the involvement of the initiator in the chain transfer stage becomes appreciable (a halogen atom is transferred from the telogen to the growing radical via an iron carbonyl intermediate—see Table 1). It has been found[39] that in the initiation by $Fe(CO)_5$, the reactivity of olefins in telomerisation with CCl_4 varies in parallel with the thermal stability of the complexes (C=C).$Fe(CO)_4$ (C=C is the monomer). Apparently a maximum $Fe(CO)_5$ concentration exists above which C_1 and C_2 no longer increase[43] and in addition self-inhibiting properties of the carbonyl make an appearance[27]. Accordingly the content of the adduct in the mixture of telomers passes through a maximum as a function of both the $Fe(CO)_5$ concentration and the reaction time at $[Fe(CO)_5]_0 = \text{const}$.[42,44,45]

The character of the initiation of the telomerisation by iron pentacarbonyl changes sharply in the presence of a nucleophilic co-initiator—an alcohol, a tertiary amine, DMF, DMSO, hexamethylphosphoramide (HMP), and *N,N*-dichloramide[27]. The first two members of the series predominate in the mixture of telomers. The chain transfer rate constant C_1 increases greatly (Table 1), which can be explained by the fact that, in the presence of a nucleophilic co-initiator incorporated in the coordination sphere of iron (this has been demonstrated by EPR[46,47]), the iron-containing species $(Fe)^nCl$, formed as a result of the abstraction of a chlorine atom from the chlorine-containing telogen (CCl_4), transfers the chlorine atom to the growing radical at a much higher rate than in the direct interaction of the growing radical with the telogen.

Table 1. The telomerisation of ethylene by carbon tetrachloride with different methods of initiation[5]*

$CCl_4 + C_2H_4 \rightarrow CCl_3(CH_2CH_2)_nCl$

Initiator	Composition of mixture of telomers, mole %					C_n			
	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	C_1	C_2	C_3	C_4
Azobisisobutyronitrile	3.1	36.2	30.9	17.2	12.5	0.15	2.8	4.9	5.5
$Fe(CO)_5$	5.4	47.3	29.0	12.7	5.9	0.20	3.6	5.7	7.9
$Fe(CO)_5 + CH_3OH$	66.7	23.7	7.8	1.8	0	6.0	7.7	13.3	—

* Temperature 100 °C; $[C_2H_4]_0/[CCl_4]_0 \cong 4$.

The rate constant for chain transfer via $Fe(CO)_4Cl$ for the adduct-radical in the telomerisation of CCl_4 with C_2H_2 and C_3H_6 using CH_3OH as the co-initiator proved to be 100 times higher than in the peroxide initiation, i.e. than in the direct interaction of the growing radical with the telogen[48,49]:

$$CCl_4 + Fe(CO)_{5-n}(CH_2OH)_n \rightarrow \dot{C}Cl_3 + ClFe(CO)_{4-n}(CH_3OH)_n + CO \ ;$$
$$\dot{C}Cl_3 + CH_2 = CH_2 \rightarrow CCl_3CH_2\dot{C}H_2 \ ;$$

$$CCl_3CH_2\dot{C}H_2 + ClFe(CO)_{4-n}(CH_3OH)_n \xrightarrow{k_{tr} \geqslant 4 \times 10^5 \text{ litre mol}^{-1}\,s^{-1}}$$
$$\rightarrow CCl_3CH_2\dot{C}H_2Cl + \dot{F}e(CO)_{4-n}(CH_3OH)_n \ ;$$
$$CCl_3CH_2\dot{C}H_2 + CCl_4 \xrightarrow{k_{tr} = 0.39 \times 10^4 \text{ litre mol}^{-1}\,s^{-1}} CCl_3CH_2CH_2Cl + \dot{C}Cl_3 \ .$$

Nucleophilic co-initiators act in two ways. On the one hand, they increase the overall rate of reaction, the rate constant increasing in parallel with the increase of their dielectric constants; on the other hand, they influence C_1, i.e. they facilitate the involvement of the initiator in the stage where the halogen is transferred from the telogen to the growing radical and can be arranged in a sequence corresponding to the increase of their electron-donating capacity[45].

The majority of systems based on $Fe(CO)_5$ effectively initiate telomerisation by chlorine-containing telogens at a temperature above 100 °C[12]. However, there exist co-initiators which significantly reduce the initiation temperature. Thus, in the presence of *N,N*-dichlorosulphonamides $XC_6H_4SO_2NCl_2$, iron pentacarbonyl effectively initiates the reaction of CCl_4 with alk-1-enes at a temperature as low as 50 °C and at 25 °C the reaction proceeds to the extent of 1–2% in 6 h.[50] In certain cases when the dissociation of the C–Hal bond is sufficiently easy, as, for example, in the case

of CBr_4 and CCl_3Br, the reaction with acrylic monomers in the presence of the usual $Fe(CO)_5$ + DMF system begins already at room temperature and takes place exothermically[51]:

$$CCl_3Br + CH_2{=}CHCOOCH_3 \xrightarrow[20-80^\circ]{Fe(CO)_5+C_6H_5N(CH_3)_2} CCl_3(CH_2\underset{\displaystyle COOCH_3}{\underset{|}{C}}H)_nBr \ ;$$

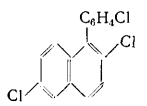
$$n = 1\,(37\%);\ n=2\,(12\%)\ .$$

It may be that in this case the carbonyl is activated by the telogen incorporated at the same time in the coordination sphere of the iron.

The use of initiating systems of the type of $Fe(CO)_5^+$ co-initiator made it possible to introduce into telomerisation compounds with the CCl_3 group[9,12,52] and benzyl chloride (via the C–Cl bond)[55]. These systems are effective in the initiation of telomerisation with participation of compounds having a CCl_2 group activated by electron-accepting substituents[53,54] and compounds with the CBr_3 and CBr_2 groups[10,56-58].

Using initiating systems based on $Fe(CO)_5$, it is possible to telomerise by polychloro- and polybromo-derivatives polymerisable monomers such as acrylic compounds[10,53,59,60], vinyl chloride[43,55,57,61], vinylidene chloride[62], and 1,3-dienes[63,64]. The familiar ability of $Fe(CO)_5$ to promote dehalogenation and dehydrohalogenation has been used in telomerisation to convert linear chain compounds into cyclic and aromatic compounds. Such are, for example, the lactonisation reactions in the telomerisation of unsaturated compounds by esters of α-halogeno-substituted acids[10] and the formation of ring-chlorinated phenylnaphthalenes in the telomerisation of DDT with vinyl chloride[65]:

$$(ClC_6H_4)_2CHCCl_3 + CH_2{=}CHCl \xrightarrow[\text{coinitiator}]{Fe(CO)_5}$$



Substituted 2,2,6-trichloro-1-(chlorophenyl)tetrahydronaphthalenes are formed in the telomerisation of ethylene, methyl acrylate, and styrene with DDT[66-68]. Thus initiators based on $Fe(CO)_5$ lead to extensive possibilities in telomerisation (see Table 6 for further details).

The representatives of the second group of metal carbonyls–chromium, molybdenum, and tungsten hexacarbonyls–give rise to an initiating metal-centred radical $\dot{M}(CO)_5$ or $L_n\dot{M}(CO)_{5-n}$; the latter abstracts a halogen atom from the telogen in the initiation stage and produces a species [for example, $ClM(CO)_5$], which is not involved in the subsequent development of telomerisation. The partial chain transfer constants C_n for the reactions of CCl_4 with ethylene and propene hardly change on passing from peroxide initiation to initiation by the carbonyls $Cr(CO)_6$, $Cr(CO)_5[P(C_6H_5)_3]$, $Mo(CO)_6$, or $W(CO)_6$[69-72] (Table 2). The formation of $\dot{C}Cl_3$ radicals in the photochemical interaction of chromium, molybdenum, and tungsten hexacarbonyls with polychloroalkanes has been demonstrated by EPR using spin trapping agents[74]. The formation of the radicals $Cl\dot{C}r(CO)_5$ by the abstraction of chlorine from CCl_4 under the influence of $Cr(CO)_6$ has also been reliably established by EPR[75,76]. The co-initiators which usually facilitate the involvement of the carbonyl-containing species in the chain transfer stage naturally do not influence the proportions of the telomers in the mixture in the given instance (where such involvement does not occur).[71] The chain transfer constants C_n are in such cases close to the "cross" constant (Table 2).

The use of co-initiators in combination with $Cr(CO)_6$ does not affect appreciably the yield of adducts and telomers in the reactions of CCl_4 and $CHCl_3$ with olefins[71,77], although the rate of initiation in the presence of a co-initiator increases (for low degrees of conversion of the telogen)[70-72]. The insertion of an active ligand of the type of $P(C_6H_6)_3$ in the ligand sphere of the metal carbonyl can increase significantly the initiating activity of the carbonyl, as has been observed for $Cr(CO)_5[P(C_6H_5)_3]$.[70] The insertion of HMP in the coordination sphere of chromium with displacement of CO and the formation of the complex $ClCr(CO)_3$(HMP) in the presence of CCl_4 has been observed by EPR[76]. Apparently metal carbonyls of this type are most effective in the initiation of telomerisation reactions which are distinguished by a long kinetic chain, because these carbonyls do not regenerate the initiating species during telomerisation.

Table 2. Partial chain transfer constants C_n for the telomerisation of propene by carbon tetrachloride with different methods of initiation (at 120 °C)[69-72].

Initiator	C_1	C_2
Peroxide*	2.65	33.0
$Cr(CO)_6$	2.63	34.9
$Mo(CO)_6$	2.03	39.2
$Mn_2(CO)_{10}$	1.79	26.4
$Cr(CO)_6$ + HMP	1.51	26.7
$Cr(CO)_6$ + DMF	1.60	28.2
$Cr(CO)_6 + CH_3CN$	1.59	22.3
$Cr(CO)_6 + CH_3OH$	1.51	23.2
$Mn_2(CO)_{10}$ + DMF	1.95	27.2

* The values obtained by interpolating the data for 95°, 105°, and 145 °C.[73]

Among the representatives of dinuclear metal carbonyls, $Mn_2(CO)_{10}$ has been studied in greatest detail in telomerisation[38,59,78-82]. The stage preceding initiation (and possibly determining the rate of reaction as a whole[27,34]) is in this instance the dissociation of the metal carbonyl at the metal–metal bond, which takes place either thermally (120–130 °C) or under the influence of ultraviolet light. The metal-centred $\dot{M}n(CO)_5$ radicals formed are capable of abstracting a chlorine atom from the telogen and of initiating telomerisation. The formation of $\dot{C}Cl_3$ from CCl_4 and of $\dot{C}Cl_2CCl_2H$ under the influence of $\dot{M}n(CO)_5$ has been demonstrated by EPR[74]. The radicals $\dot{M}n(CO)_5$ cannot then be attached to a spin trapping agent, which indicates a high reactivity in the abstraction of chlorine from the telogen[74]. The partial chain transfer constants for the telomerisation of ethylene and propene with CCl_4, initiated by $Mn_2(CO)_{10}$, are close in magnitude to the chain transfer constants for the same reaction initiated by peroxides[82] (Table 2). The relative isomerisation constant in the reaction of methyl chloroacetate with ethylene, initiated by $Mn_2(CO)_{10}$, is almost the same as under the conditions of peroxide initiation[38]. The main process stabilising the growing adduct and telomer radicals is abstraction of hydrogen by the latter from the components of the medium [pathway (2), Scheme 2].

Thus the available data show that $Mn_2(CO)_{10}$ does not participate in the stage involving the transfer of the halogen from the telogen to the growing radical[38,59,80-82]. It does not initiate the addition of CH_3OCOCH_2R to hex-1-ene which takes place effectively in the presence of peroxides[81] whence it follows that $\dot{M}n(CO)_5$ does not participate in the transfer of hydrogen from the substrate to the growing radical, accompanied by the dissociation of a C–H bond. (This does not apply to processes involving the homolysis of other E–H bonds, for example Si–H.) It has been found that $Mn_2(CO)_{10}$ initiates fairly readily reactions with both CCl_4 and $RCCl_3$[59,79,80], since in its presence telomers with the CCl_3 group are

capable of further reactions of the type of stepwise telomerisation (see Section VI). This property of $Mn_2(CO)_{10}$ apparently explains the maxima on the curve describing the time variation of the yields of the lower telomers[80].

A characteristic feature of $Mn_2(CO)_{10}$ as an initiator is that nucleophiles not only do not activate it but in many instances actually reduce the effectiveness of initiation[79,80]. Microadmixtures of iron compounds exert a considerable influence; therefore, when telomerisation initiated by $Mn_2(CO)_{10}$ is carried out in metallic reactors, i.e. under conditions close to those obtained in the industrial process, one can obtain a mixture of telomers with an increased content of lower telomers, which is reflected in the chain transfer constant determined[36,83].

It is noteworthy that, in the telomerisation of ethylene by methyl chloroacetate, initiation proceeds with abstraction of the chlorine atom by the $Mn(CO)_5$ radicals, but the overall reaction product is almost wholly a mixture of telomers formed as a result of the dissociation of a C–H bond in the telogen[38]:

$$\left.\begin{array}{l} CH_3OCOCH_2Cl \xrightarrow{Mn_2(CO)_{10}} CH_3OCO\dot{C}H_2 \xrightarrow{nC_2H_4} \dot{T}_n \\ \dot{T}_n \xrightarrow{CH_3OCOCH_2Cl} CH_3OCO\dot{C}HCl \end{array}\right\} \text{(initiation);}$$

$$\left.\begin{array}{l} CH_3OCO\dot{C}HCl + n\,H_2C=CH_2 \rightarrow CH_3OCOCHCl(CH_2CH_2)_n\dot{} \\ CH_3OCOCHCl(CH_2CH_2)_n\dot{} + ClCH_2COOCH_3 \rightarrow \\ \rightarrow CH_3OCOCHCl(CH_2CH_2)_nH + CH_3OCO\dot{C}HCl \end{array}\right\} \text{(main kinetic chain).}$$

The telomerisation of ethylene[38,80–82] and propene[82] with CCl_4, of ethylene with CCl_3COOCH_3[38] and $ClCH_2COOCH_3$[38,81], and of 1,1,1,3-tetrachloropropane with methyl acrylate[59] can be initiated with the aid of $Mn_2(CO)_{10}$.

IV. STEPWISE TELOMERISATION

A telomer having a group reactive in telomerisation (CCl_3, CBr_3) can play the role of a telogen, having entered into a secondary reaction with the monomer. Such a process has come to be called stepwise[12] or secondary[4] telomerisation, in contrast to the usual chain telomerisation. The products of the stepwise telomerisation can have the same structure as the telomers obtained by the usual (chain) telomerisation if the carbon atom which carries the unpaired electron in the growing radical is attacked in the secondary reaction[84]:

$$CH_3I \xrightarrow{C_2H_4} CH_3CH_2CH_2I \xrightarrow{C_2H_4} CH_3(CH_2)_4I \text{ etc.}$$

The synthetic value of this reaction consists in the fact that any telomer-homologue can be obtained from preceding members of the series by consecutive monomer addition steps.

The structure of the product of the stepwise telomerisation can, however, differ from that of the telomers obtained by the usual telomerisation when there are several reactive centres in the telomer and the radical attack is not directed to the carbon atom carrying the unpaired electron in the growing radical[85]:

$$CH_3OCOCH\underset{\downarrow}{Br}_2 \xrightarrow{CH_2=CHCl} CH_3OCOCH\underset{\downarrow}{Br}CH_2CHClBr \xrightarrow{CH_2=CHCl} \rightarrow CH_3OCOCH(CH_2CHClBr)_2 .$$

(The arrow indicates the point of attack.) This version of the stepwise telomerisation makes it possible to synthesise branched telomers†. The greatest synthetic possibilities in this version arise from the application of coordination initiators (including metal carbonyls), which initiate selectively the reaction at the most reactive C–Hal bond in the telogen[12]. However, stepwise telomerisation is also not ruled out for peroxide initiation[56,86]:

$$CBr_4\ (\text{or } CHBr_3) \xrightarrow[BP]{C_2H_4} CBr_3CH_2CH_2Br \xrightarrow[BP]{C_2H_4} (BrCH_2CH_2)_2CBr_2 ,$$

where BP is benzoyl peroxide. 1,1,1,3-Tetrachloroalkanes enter into the stepwise telomerisation initiated by the $Fe(CO)_5$ + co-initiator systems[9,87,88], for example:

$$ClCH_2CH_2CCl_3 + C_2H_4 \rightarrow (ClCH_2CH_2)_2CCl_2 .$$

When the esters of α-halogeno-substituted acids are used as telogens, the stepwise telomerisation makes it possible to obtain α-substituted lactones[89], including spiro-dilactones, which are difficult to obtain by other procedures[90]:

$$CHCl_2COOCH_3 + 2\,C_2H_4 \rightarrow \begin{array}{l} H_2C\text{——}CClCH_2CH_2Cl \\ \quad|\qquad\quad| \\ H_2C\quad C{=}O \\ \quad\diagdown O\diagup \end{array} ;$$

$$(C_2H_5OCO)_2CBr_2 + 2\,RCH=CH_2 \rightarrow \begin{array}{l} \quad\quad\quad\quad\quad\quad\quad\quad O \\ \quad\quad\quad\quad\quad\quad\quad\quad \downarrow \\ RHC\text{—}C\quad\quad C\text{—}O \\ \quad|\quad\quad\quad\quad| \\ O\text{—}C\quad\quad C\text{—}CHR \\ \quad\quad\diagdown\quad\quad\diagup\ (\ H_2) \\ \quad\quad\quad C \\ \quad\quad\quad\quad O \end{array} .$$

Thus the stepwise scheme expands the synthetic possibilities of telomerisation.

1. Determination of the Structure of Halogen-containing Telomers

In all cases of telomerisation with participation of polyhalogeno-telogens, it is necessary to solve problems involving the determination of the structure of the telomers, which are sometimes by no means simple, bearing in mind the possibility of rearrangements in the growing radicals, of the disproportionation of the halogens in the chlorine- and bromine-containing adducts and telomers[91], and the probability of stepwise telomerisation. Studies in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Synthesis of the USSR Academy of Sciences[92–99] have established that ^{13}C NMR is a reliable method for the determination of the structures of polyfunctional halogen-containing telomers. The regions in which the signals of various polychloro-groups[92–95] and polybromo-groups[95–97] appear have been investigated in detail, the characteristic interactions of the vicinal and geminal halogen atoms have been discovered, and a scheme has been developed using the additive increments due to chlorine and bromine in the chlorine- and bromine-containing fragments[98,99], which makes it possible to calculate the chemical shifts of the polyhalogeno-groups in the ^{13}C NMR spectra.

V. TELOMERISATION ACCOMPANIED BY THE REARRANGEMENT OF THE RADICALS

Oxygen-containing telogens reacting as a result of the dissociation of a C–H bond are of special interest in the telomerisation reaction. These include carboxylic acids, alcohols, ketones, and their various derivatives (Table 3). These telogens have been investigated in reactions with a wide range of monomers, which has led to the discovery of the characteristics of the telomerisation with their participation, involving the rearrangement of the growing radicals.

† In this case the usual telomers have the structure $CH_3OCOCHBr(CH_2CHCl)_nBr$.

As a result, the growing radical in this group of reactions participates simultaneously in three competing processes—chain propagation, chain transfer, and isomerisation. The study of the characteristics of such reactions has demonstrated extensive possibilities in their employment for research and synthetic purposes[11,100,101].

Table 3. The telomerisation of unsaturated compounds by carboxylic acids and their derivatives, alcohols, ketones, and acetals.

No.	Telogen	Identified telomers*	n, m	$10^2\ C_{n\geq 3}$	C_i (type of migration)	Refs.
		Monomer $CH_2=CH_2$; $R=C_4H_9$				
1	HCO_2CH_3	$H(CH_2CH_2)_nCO_2CH_3$	1—4	17	—	[111]
		$HO_2CCH_2(CH_2CH_2)_nH$	1—3	15	—	
		$H(CH_2CH_2)_nCH(CH_2R)CO_2CH_3$	1—2	8	9.4 (1.6-H)	
2	CH_3CO_2H	$H(CH_2CH_2)_nCH_2CO_2H$	1—4	—	—	[102]
		$H(CH_2CH_2)_mCHRCO_2H$	1—2	—	(1.5-H)	[104]
3	$CH_3CO_2CH_3$	$H(CH_2CH_2)_nCH_2CO_2CH_3$	1—6	4	—	
		$CH_3CO_2CH_3(CH_2CH_2)_nH$	1—3	—	—	
		$H(CH_2CH_2)_mCHRCO_2CH_3$	1—3	6	1.5 (1.5-H)	
4	CH_3CN	$H(CH_2CH_2)_nCH_2CN$	1—4	4	—	[109]
		$H(CH_2CH_2)_mCHRCN$	1—2	3	0.9 (1.5-H)	
5	$ClCH_2CO_2CH_3$	$H(CH_2CH_2)_nCHClCO_2CH_3$	1—4	20	—	[105]
		$H(CH_2CH_2)_mCClRCO_2CH_3$	1—2	16	3.6 (1.5-H)	
6	$BrCH_2CO_2CH_3$	$Br(CH_2CH_2)_nCH_2CO_2CH_3$	1—4	120	0	[108]
7	$CH_3CH_2CO_2H$	$H(CH_2CH_2)_nCH(CH_3)CO_2H$	1—5	15	—	[107]
		$H(CH_2CH_2)_mCR(CH_3)CO_2H$	1—2	19	6.5 (1.5-H)	
8	$CH_3CH_2CO_2CH_3$	$H(CH_2CH_2)_nCH(CH_3)CO_2CH_3$	1—4	12	—	[106]
		$H(CH_2CH_2)_mCR(CH_3)CO_2CH_3$	1—2	13	5.2 (1.5-H)	
9	CH_3CH_2CN	$H(CH_2CH_2)_nCH(CH_3)CN$	1—4	8	—	[103]
		$H(CH_2CH_2)_mCR(CH_3)CN$	1—2	11	2.9 (1.5-H)	
10	$C_4H_9CH_2CO_2CH_3$	$H(CH_2CH_2)_nCH(C_4H_9)CO_2CH_3$	1—4	14	—	[103]
		$H(CH_2CH_2)_mCR(C_4H_9)CO_2CH_3$	1—2	12	2.0 (1.5-H)	
11	$C_4H_9CH_2CN$	$H(CH_2CH_2)_nCH(C_4H_9)CN$	1—3	—	—	[132]
		$CH_3CH_2CR(C_4H_9)CN$	1		(1.5-H)	
12	$CH_3COCH_2CO_2CH_3$	$H(CH_2CH_2)_nCH(COCH_3)CO_2CH_3$	1—2	—	—	[133]
		$CH_3CH_2CR(COCH_3)CO_2CH_3$	1	—	(1.5-H)	
13	ClCOCOCl	$Cl(CH_2CH_2)_nCOCl$	1—3	700	(1.5-Cl)	[134]
14	$CH_2(CO_2CH_3)_2$	$H(CH_2CH_2)_nCH(CO_2CH_3)_2$	1—2	—	—	[135]
		$H(CH_2CH_2)_mCR(CO_2CH_3)_2$	1—2	—	(1.5-H)	
15	$NCCH_2CO_2CH_3$	$H(CH_2CH_2)_nCH(CN)CO_2CH_3$	1—6	—	—	[136]
		$H(CH_2CH_2)_mCR(CN)CO_2CH_3$	1—4	—	43 (1.5-H)	
16	$CH_3O_2C(CH_2)_kCO_2CH_3$ ($k=2,4$)	$H(CH_2CH_2)_nCH(CH_2)_{k-1}CO_2CH_3$ $\quad\quad\quad

Table 3 (contd.)

No.	Telogen	Identified telomers*	n, m	$10^2 C_{n\geqslant 3}$	C_i (type of migration)	Refs.
		Monomer $CH_2=CHCl$				
27	$ClCH_2CO_2CH_3$	$H(CHClCH_2)_nCHClCO_2CH_3$	1–3	—	—	[117]
		$ClCH_2O_2CCH_2(CH_2CHCl)_mH$	1–2	—	0	
28	$CH_3CH_2CO_2CH_3$	$H\,CHClCH_2)_nCH(CH_3)CO_2CH_3$	1–2	—	0	[118]
		Monomer $(CH_3)_2C=CH_2$				
29	$ClCH_2CO_2CH_3$	$H[(CH_3)_2CCH_2]_nCHClCO_2CH_3$	1–2	—	—	[123]
		$H[(CH_3)_2CCH_2]_2CClCO_2CH_3$	2	—	(1,5-H)	
		$CH_2C(CH_3)=CH_2$				
		$CH_2=C(CH_3)CH_2[(CH_3)_2CCH_2]_mCHClCO_2CH_3$	0–1		—	
30	$CH_3CH_2CO_2CH_3$	$H[(CH_3)_2CCH_2]_nCH(CH_3)CO_2CH_3$	1–2	—	—	[24]
		$H[(CH_3)_2CCH_2]_2C(CH_3)CO_2CH_3$	2	—	(1,5-H)	
		$CH_2C(CH_3)=CH_2$				
		Monomer $C_4H_9CH=CH_2$				
31	$ClCH_2CO_2CH_3$	$H(C_4H_9CHCH_2)_nCHClCO_2CH_3$	1–2	—	—	[121]
		$(C_4H_9CH_2CH_2)_2CClCO_2CH_3$	2	—	(1,3-H)	
32	$CH_3CH_2CO_2CH_3$	$H(C_4H_9CHCH_2)_nCH(CH_3)CO_2CH_3$	1–2	—	—	[121]
		$(C_4H_9CH_2CH_2)_2C(CH_3)CO_2CH_3$	2	—	(1,3-H)	
		Monomer $CH_3CO_2CH=CH_2$				
33	$CH_3CH_2CO_2CH_3$	$H(CH_3CO_2CHCH_2)_nCH(CH_3)CO_2CH_3$	1–3	—	—	[119]
		$H(CH_3CO_2CHCH_2)_2CX(CH_3)CO_2CH_3$	2	—	(1,5-H)	
		(X=$CH_3CO_2CH_2CH_2$, $CH_3CHCO_2CH_3$)				
		Monomer $CH_3CO_2CH_2CH=CH_2$				
34	$CH_3CH_2CO_2CH_3$	$H(CH_3CO_2CH_2CHCH_2)_nCH(CH_3)CO_2CH_3$	1–3	—	—	[120]
		$(CH_3CO_2CH_2CH_2CH_2)_2C(CH_3)CO_2CH_3$	2	—	(1,3-H)	
		Monomer $(CH_3)_3SiCH=CH_2$				
35	$CH_3CH_2CH_3$	$H[(CH_3)_3SiCHCH_2]_nCH(CH_3)CO_2CH_3$	1–2	—	—	[122]
		$[(CH_3)_3SiCH_2CH_2]_2C(CH_3)CO_2CH_3$	2	—	(1,3-H)	

* Here R is an alkyl group appearing in the α-position relative to the functional group as a result of the rearrangement of the radicals and chain propagation in accordance with Scheme 8.

1. Reaction Conditions

The low effectiveness of the telogens reacting as a result of the dissociation of a C–H bond as chain transfer agents in the reaction makes it necessary to employ as initiators mainly alkyl or acyl peroxides, which give rise to RO· radicals on decomposition (t-butyl peroxide, dicyclohexyl peroxydicarbonate) in the temperature range 50–150 °C. These reactions are characterised by relatively low degrees of conversion of the telogen (1–10%) and sometimes the formation of a considerable amount (15–60%) of unidentified higher telomers. In order to reduce the content of the latter, the telomerisation must be carried out at comparatively low pressures (25–50 atm). Analytical and preparative gas–liquid chromatography and ^1H and ^{13}C NMR spectroscopy are widely used to analyse the mixtures, to obtain the telomers in a pure form, and to demonstrate their structure.

2. Telomerisation of Ethylene

It was demonstrated for the first time in 1964 that the telomerisation of ethylene by acetic acid (Table 3, No.2) is accompanied by a rearrangement of the growing radicals with 1,5-migration of the hydrogen atom, which leads to the formation of two series of telomers[102]. Subsequently, it was possible to show in relation to a wide range of reactions with ethylene that such rearrangement is a fairly common phenomenon for reactions with comparatively ineffective telogens[103] (Scheme 8). The radicals (C) formed in the initiation stage react with ethylene to produce the growing radicals (D), which are converted into telomers of the non-rearranged series T_n, having transferred the chain to the telogen:

Scheme 8

$$\underset{(T_0)}{RCH_2CO_2CH_3} + R'O^{\cdot} \rightarrow \underset{(B)}{R\dot{C}HCO_2CH_3}\ ;$$

$$\underset{(C)}{\cdot} + n\,CH_2=CH_2 \rightarrow \underset{(D)}{\cdot(CH_2CH_2)_n\,CHRCO_2CH_3}\ ;$$

$$(D) \xrightarrow{T_0} H(CH_2CH_2)_nCHRCO_2CH_3\ ;$$

$$\dot{C}H_2CH_2CH_2CH_2CHRCO_2CH_3 \xrightarrow{1,5\text{-H-rearrangement}} \underset{(F)}{CH_3CH_2CH_2CH_2\dot{C}RCO_2CH_3} \rightarrow$$

$$\xrightarrow{C_2H_4} CH_3(CH_2)_3CRCO_2CH_3 \xrightarrow{T_0} \underset{T_m}{H(CH_2CH_2)_m\,CRCO_2CH_3}\ .$$

$$\quad\quad\quad

It has been shown[103] that in the given system the growing radical (D) ($n = 1$) does not rearrange with 1,3-migration of hydrogen. It might have been supposed that telomers with a branched structure T'_m are obtained via the stepwise telomerisation mechanism from the telomers formed (see Section IV). However, detailed investigations yielded much evidence showing that here we are in fact dealing with a rearrangement of radicals[11]. One of the most convincing pieces of evidence is the high process selectivity—only one series of branched telomers containing the butyl group in the α-position is formed. Special tests demonstrated the absence of comparable amounts of α-ethyl-substituted telomers, which should have been produced as a result of the secondary reaction of the first telomer $CH_3CH_2CHRCO_2CH_3$ with ethylene[11].

The influences of various factors on the course of telomerisation and on the degree of rearrangement have been estimated quantitatively in relative terms and compared using the method of relative kinetics, within the framework of which the partial chain transfer constants $C_n = k_{tr}/k_p$ and the relative isomerisation constants $C_i = k_i/k_p$ have been estimated (Table 3).[103] For the same monomer, when the radical centre is sufficiently remote from the functional group and the substituent R, the reactivity of the radicals $\dot{C}(CH_2CH_2)_nCHRCO_2CH_3$ is independent of the nature of R. The difference between the values of C_n with $n \geq 3$ for reactions involving different telogens $RCH_2CO_2CH_3$ is then determined solely by the difference between the efficiencies of the telogens as chain transfer agents for the reaction (Table 3). Thus $C_{n\geq 3}$ can serve as a relative measure of the efficiency of the given telogen in the chain transfer stage. The data in Table 3 show that the telogens investigated in telomerisation with ethylene, which react at the C–H bond, are characterised by extremely low values of $C_{n\geq 3}$ (from 0.04 to 0.20) and only methyl bromoacetate (Table 3, No.6), which reacts as a result of the dissociation of the C–Br bond, can be classified as an extremely effective telogen.

The corresponding radicals differ much more as regards the degree of rearrangement C_i. $C_i = 0$ has been obtained for methyl bromoacetate, which is highly effective in telomerisation. Comparison of data for methyl acetate and methyl bromoacetate (Table 3, Nos.3 and 6 respectively), where the growing radicals are the same, has shown that a higher value of C_i corresponds to the less effective methyl acetate. Thus the comparatively low efficiency of the telogen in the chain transfer reaction constitutes an important condition for the rearrangement of the radicals.

However, this is a necessary but not a sufficient condition. Thus the values of $C_{n\geq 3}$ for methyl chloroacetate (No.5) and methyl propionate (No.8) are higher than for methyl acetate (No.5) and the degree of rearrangement is in this case also higher (see Table 3). In the given instance, the difference between the stabilities of the initial and rearranged radicals plays a significant role and it is naturally higher in the presence of a substituent R = Cl or CH_3, different from hydrogen, at the radical centre of the rearranged radical (F) (Scheme 8). Here the polar nature of the substituent R does not play a fundamental role: for both electron-donating (CH_3) and electron-accepting (Cl) substituents, the degree of rearrangement is higher than for R = H.

On the other hand, the increase of the chain length of the substituent in the α-position relative to the carboxy-group (Table 3, No.10) results in a decrease of the degree of rearrangement, which can be explained by the appearance of steric hindrance in the intramolecular chain transfer stage. At the same time the nature of the initiating system [peroxides and complex initiators based on $Mn_2(CO)_{10}$ and $Fe(CO)_5$] hardly affects the rearrangement with migration of hydrogen in the telomerisation reaction[36,62,82].

3. Telomerisation of Propene

The replacement of ethylene by propene led to new prospects for the investigation of telomerisation (Scheme 9). In the study of the telomerisation of propene by carboxylic acids and their derivatives, it was shown[11] that, together with the 1,5-migration of hydrogen in the radical (H), there is also a high degree of the 1,3-migration of hydrogen in the radical (G) containing one monomer unit. This results in a sharp increase of the content of telomers with two substituents in the α-position and among the higher telomers there are virtually no compounds of the non-rearranged series[112–114] (Table 3, Nos.23, 24, and 26).

Scheme 9

$$\underset{(G)}{CH_3\dot{C}HCH_2CHRCOOCH_3} \xrightarrow{1,3\text{-H}} \underset{(G')}{CH_3CH_2CH_2\dot{C}RCOOCH_3}\ ;$$

$$\underset{(H)}{CH_3\dot{C}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_2CHRCOOCH_3} \xrightarrow{1,5\text{-H}} \underset{(H')}{CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}H\dot{C}RCOOCH_3}.$$

Comparison of data for the reactions of propene with various telogens of the type $RCH_2CO_2CH_3$ (R = H, Cl, or CH_3)[112,113,115] shows that in this series too the lowest relative degree of rearrangement corresponds to methyl acetate (R = H), where the difference between the stabilities of the rearranged (H′) and non-rearranged (H) radicals is smallest (see Scheme 9). It has been shown in relation to the telomerisation of propene by methyl chloroacetate (Table 3, No.24)[114,116] that the decrease of the reaction temperature from 150 °C to 25 °C results in the disappearance of the telomers whose formation is associated with the 1,3-migration of hydrogen, while the 1,5-migration of a hydrogen atom, which is more favourable from the standpoint of the conformation of the transition state, proved to be much less affected by the change of temperature. This is yet another piece of evidence showing that we are in fact dealing with the migration of hydrogen, since in the case of the secondary reaction of telomers T_n of the type $H[CH(CH_3)CH_2]_nCHRCO_2.CH_3$ with propene there are no grounds for expecting markedly different reactivities for T_1 and T_2.

The rearrangement of the radicals with 1,3-migration of hydrogen in the case of propene is associated, in our view, with a favourable combination of polar factors—the nucleophilic radical centre attacks the electrophilic component of the radical in the intramolecular transfer range.

4. Other Monomers

The significant role of the polar characteristics of the growing radical in the rearrangement has been confirmed in the study of the telomerisation of vinyl chloride (Table 3, Nos.27 and 28), where the growing radicals have a pronounced electrophilic character. In this case the rearrangement of the radicals $Cl\dot{C}HCH_2(CHClCH_2)_nCHRCO_2CH_3$, where $n = 0$, 1, does not occur[117,118].

The influence of the nature of the monomer on the reaction has been manifested also in the comparison of the results obtained in the reactions of methyl propionate with vinyl acetate[119] and allyl acetate[120] (Table 3, Nos.33 and 34). In the former case only the 1,5-migration of a hydrogen atom takes place, while in the reaction with $CH_2{=}CHCH_2CO_2CH_3$, which can be regarded as a substituted analogue of propene,

the 1,3-migration of hydrogen takes place. The formation of two telomers with different structures containing two monomer units was also noted for the telomerisation of hex-1-ene[121] (Table 3, Nos.31 and 32) and trimethylvinylsilane[122] (No.35).

A number of interesting features distinguish the telomerisation of isobutene[24,122]. In this case there is no 1,3-migration of hydrogen in the radical $(CH_3)_2\dot{C}CH_2CHRCO_2CH_3$, although polar factors favour it (see Scheme 10). The absence of the rearrangement is apparently associated with the steric hindrance, which has a particularly marked effect in the stage involving the formation of the energetically unfavourable four-membered transition state, while the 1,5-migration of hydrogen in the radical (I) proceeds to a high extent:

Scheme 10

$$(CH_3)_2\dot{C}CH_2C(CH_3)_2CH_2CHRCO_2CH_3 \xrightarrow{1,5\text{-}H} (CH_3)_2CHCH_2C(CH_3)_2CH_2\dot{C}RCO_2CH_3$$

(I) (I')

$$(CH_3)_2C{=}CH_2 \longrightarrow CH_3C(\dot{\ })(=CH_2)_2 \ ;$$

$$(I') + CH_3C(\dot{\ })(=CH_2)_2 \longrightarrow (CH_3)_2CHCH_2C(CH_3)_2CH_2CRCO_2CH_3 \longrightarrow$$

$$\longrightarrow (CH_3)_2CHCH_2C(CH_3)_2CH_2CRCO_2CH_3 \ .$$

$$CH_2CH(CH_3)_2$$

Here the behaviour of the radical (I') is unusual. By virtue of the characteristic features of its structure, it is hardly involved in the chain propagation and transfer reactions and mainly recombines with the isobutenyl radicals, giving rise to an unsaturated compound. Subsequently the hydrogenation of the double bond makes it possible to obtain readily the saturated analogue.

5. Telomerisation of Olefins by Acetals

The study of the telomerisation of ethylene[124] and propene[125] by linear acetals led to the discovery of a new combination of rearrangements with 1,5- and 1,9-migrations of a hydrogen atom (Table 3, No.18). The reaction develops via the C–H bond of the methoxy-group with formation of long-chain acetals T_n. The intermediate growing radicals (Scheme 11) with one and three monomer units rearrange respectively with 1,5- and 1,9-migration of hydrogen. On the other hand, the radical with two monomer units does not rearrange with 1,7-migration of hydrogen. Such selectivity constitutes important evidence in support of an intramolecular character of the migration of hydrogen, because all three telomers T_n, where n = 1, 2, and 3, can participate to equal extents in secondary reactions. We may note that the 1,9-migration of hydrogen corresponds to two 1,5-transitions as regards the conformation of the transition state, which probably actually facilitates the occurrence of this rearrangement[126]:

Scheme 11

$$CH_3CH(OCH_3)_2 \xrightarrow{R\dot{O}} CH_3\dot{C}H(OCH_3)OCH_2 \ ;$$

(T_0)

$$CH_3\dot{C}H(OCH_3)OCH_2 + n\,CH_2{=}CH_2 \xrightarrow{T_0} CH_3CH(OCH_3)OCH_2(CH_2CH_2)_nH \ ;$$

(T_n)

$$CH_3CH(OCH_3)OCH_2(CH_2\dot{C}H_2)_n \xrightarrow[1,9\text{-}H(n=3)]{1,5\text{-}H(n=1)} CH_3\dot{C}(OCH_3)OCH_2(CH_2CH_2)_nH \ ;$$

$$CH_3\dot{C}(OCH_3)OCH_2(CH_2CH_2)_nH \xrightarrow[-CH_3\dot{O}]{} CH_3C(O)OCH_2(CH_2CH_2)_nH \ .$$

6. The Use of ^{13}C NMR for the Investigation of the Structure of Telomers

The processes described above and analogous reactions always result in the formation of extremely complex compounds having a branched structure and belonging to different classes—carboxylic acids and their esters, nitriles, halogeno-derivatives, substituted cyclic and linear acetals and their hetero-analogues, etc. ^{13}C NMR has been used widely and successfully to determine the structures of such compounds[121,127–131]. The characteristic groups and the corresponding chemical shifts of the signals as well as the rules governing the variation of the chemical shifts as a function of the structure of neighbouring units have been discovered for a large number of model compounds. For example, the ^{13}COO and $^{13}CH_3$–C signals are displaced downfield with increase of the number of substituents at the neighbouring carbon atom; the accumulation of substituents at the β-carbon atom leads to an upfield shift of the $^{13}CH_3$.CH_2C signal. Calculations based on an additive scheme taking into account corrections[128] and the regression equation proposed by ourselves, with the corresponding coefficients, which relates the chemical shifts of the key signals of the test compounds, in particular, the esters of polybranched acids, to the chemical shifts of the signals of the corresponding carbon atoms in isostructural hydrocarbons, have been widely used to assign the signals[121,129].

VI. COTELOMERISATION OF TWO MONOMERS WITH ONE TELOGEN

Cotelomerisation may imply the reactions of two monomers with one telogen, of two telogens with one monomer, or of two monomers with two telogens[4,12]. The study of cotelomerisation was begun only in recent years and concerns mainly different versions of the reactions of monomers with one telogen. The difficulties in the study of a complex mixture of homo- and co-telomers limit the development of this field. Examination of the simplest cotelomerisation scheme

$$\underbrace{X-Y}_{\text{telogen}} + \underbrace{mA + nB}_{\text{monomers}} \xrightarrow{\text{initiator}} \underbrace{XA_mB_nY}_{\text{cotelomers}} \ ,$$

shows that, for each value of the sum $m + n$, one may expect the formation of 2^{m+n} different structures if the growth of the radical chain takes place only via the "head to tail" mechanism. When $m + n = 1–3$, there is a possibility of the formation of 14 compounds; the absence of asymmetric atoms in the molecules of the products is then assumed.

Table 4. The cotelomerisation of two monomers* with one telogen.

No.	Monomer	Telogen	Initiator	Identified cotelomers T_n		Refs.
				$n=2$	$n=3,4$	
1	$CH_2=CH_2+CH_2=CHCH_3$	CCl_4	$(C_6H_5CO)_2O_2$	T_2^{PE}, T_2^{EP}	$T_3^{PEE}, T_3^{EEP}, T_3^{PEP}$	[143]
2	$CH_2=CH_2+CH_2=CHCH_3$	$(CH_3)_2CHCOOCH_3$	$[(CH_3)_3C]_2O_2$	T_2^{PE}, T_2^{EP}	**	[144]
3	$CH_2=CH_2+CH_2=C(CH_3)_2$	$(CH_3)_2CHCOOCH_3$	$[(CH_3)_3C]_2O_2$	T_2^{EI}, T_2^{IE}	**	[145]
4	$CH_2=CH_2+CH_2=CHCl$	CCl_4	$(C_6H_5CO)_2O_2$	T_2^{VE}, T_2^{EV}	T_3^{VEE}, T_3^{EVE}	[146, 147]
5	$CH_2=CHCH_3+CH_2=CHCl$	$CHCl_3$	$(C_6H_5CO)_2O_2$	T_2^{VP}, T_2^{PV}	T_3^{VPV}, T_3^{PVP}	[148]
6	$CH_2=CHCH_3+CH_2=CHCl$	CCl_4	$(C_6H_5CO)_2O_2$	T_2^{VP}, T_2^{PV}	$T_3^{PVP}, T_3^{PPV}, T_3^{VVP}, T_3^{VPV}$	[149, 150]
7	$CH_2=CHCH_3+CH_2=CCl_2$	CH_3CCl_3	$Fe(CO)_5$ + DMF	T_2^{VP}	Not investigated	[151]
8	$CH_2=CHCH_3+CH_2=CHCN$	CCl_4	$[(CH_3)_3C]_2O_2$	T_2^{PA}, T_2^{AP}	Not investigated	[152]
9	$CH_2=CH_2+CF_2=CFCF_3$	FSO_2Cl	$(C_6H_5CO)_2O_2$	Not formed	T_3^{EFE}, T_4^{EFEE}	[153]

* Conventional notation: $E = CH_2CH_2$, $P = CH_2CHCH_3$, $I = CH_2C(CH_3)_2$, $V = CH_2CHCl$, $V' = CH_2CCl_2$, $A = CH_2CHCN$, $F = CF_2CFCF_3$.
** All possible telomers have been obtained.

In view of the difficulties in the investigation, cotelomerisation was initially used only to obtain mixtures of oligomers with useful properties—fire resistance, thermal stability, high covering power, and compatibility with polymers. Numerous examples of the preparation of such oligomers have been published[4]; the molecular weights of a series of these, which varies in the range from 400 to 10000, were indicated.

The study of the structure of the lower cotelomers and the determination of the ratio of their yields and the yields of homotelomers as a function of the reaction conditions and the nature of the components are of great theoretical interest. Such study makes it possible to investigate the comparative reactivities of the monomers and radicals in competing reactions, to determine the sequence in which the monomer units are incorporated in the radical chain, and to observe the influence of the polar properties of the monomers, telogens, and growing radicals on the reactions. Cotelomerisation can apparently be used as a model for the solution of certain problems in copolymerisation.

The cotelomerisation of different pairs of monomers with telogens reacting both via a C–Cl bond (Table 4, Nos.1, 4, 6, 7, and 8), via a C–H bond (Nos.2, 3, and 5), or via an S–Cl bond (No.9) was investigated for the first time in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Compounds of the USSR Academy of Sciences in relation to nine examples (Table 4) with identification of all the homotelomers and cotelomers formed, containing between one and three monomer units in the molecules. In examples 1–3 both monomers are olefins and are characterised by a polar effect of the same kind; in the remaining examples each two monomers differ markedly as regards the polar effect.

Table 4 shows that in all cases, except for Nos.7 and 9, both possible cotelomers, containing two monomer units, were obtained; the cotelomer whose formation is favoured by the polar effect in the chain transfer stage and by the higher reactivity of the radical centre in T_2 is then formed in a higher yield. When the polar effects of the two monomers act in the same direction and when the telogen is weakly electrophilic, all six possible cotelomers, containing three monomer units, are formed (Nos.2 and 3). In all the remaining cases the cotelomers T_2, for which the polar effect is unfavourable in the chain propagation or chain transfer stage (Nos.1 and 4–6), are not formed. Example 9 is a special case where the two monomers not only differ in their polarity but one of them ($CF_2=CF-CF_3$) is extremely inert in radical reactions; nevertheless it has been possible to involve perfluoropropene in this process. Here it is easy to observe the influence of the polar effects—the absence of groups of the type FSO_2F_n and FSO_2EFF.

VII. PROSPECTS FOR THE PRACTICAL APPLICATION OF TELOMERISATION

The study of the chemical reactions of the tetrachloroalkanes $CCl_3(CH_2CH_2)_nCl$ demonstrated the possibility of using them for the synthesis of ω-chlorocarboxylic acids on the basis of which methods have been developed for the preparation of a new polyamide fibre and synthetic perfumes[1,154]. The reaction of ethylene with tetrachloroethylene made it possible to synthesise 1,1,2-trichlorobutadiene, which readily polymerises via a radical mechanism; its polymers are readily soluble in organic solvents, are resistant to the action of inorganic acids in the cold, and are incombustible; their films exhibit an effective adhesion to metals, rubber, and synthetic materials[155].

The telomerisation of ethylene via the esters of halogenoacetic acids has served as the basis of a method for the synthesis of γ-aminobutyric and ε-aminocaproic acids; the former is an active psychotropic preparation (Gammalon) and the latter is an agent arresting the flow of blood (ε-Capron)[156,157].

The telomerisation of DDT in the presence of complex initiators with formation of derivatives of tetra- and dihydronaphthalenes constitutes one of the possible procedures for the chemical treatment of DDT.[158] Alkyl chlorides, which are essential for the manufacture of biologically degradable surfactants, are obtained by the telomerisation of ethylene by hydrogen chloride. Preparations have been made for the industrial application of this process[159].

The combination in a single process of telomerisation and the rearrangement of radicals made it possible, after a suitable selection of the monomers, telogens, and process parameters, to devise a simple single-stage method of synthesis of branched and polybranched monocarboxylic acids (VIK, PORK), which produce no chemical waste or waste water. The method makes it possible to obtain acids with a wide variation of their structures within the framework of a single universal technology. The preparation of branched

Table 5. Examples of the telomerisation of unsaturated compounds by halogen-containing telogens initiated by organic radical-forming agents.

No.	Telogen (bond dissociated)	Monomer	Initiator and reaction conditions	Identified telomers and (C_n)	n	Refs.
1	$CHCl_3$(C—Cl, C—H)	CH_2=CHC_3H_7	TBP; 3 h 130—150°	$CCl_3(CH_2CHC_3H_7)_nH$	1—2	[166]
				$CCl_3CH_2CHClC_3H_7$	—	
				$CHCl_2CH_2CH_2C_3H_7$	—	
				$CHCl_2CH_2CHClC_3H_7$	—	
2	$CHBr_3$(C—Br)	CH_2=CH_2	BP; 4 h, 100°	$CHBr_2(CH_2CH_2)_nBr$	1—2	[56]
3	$CHBr_3$(C—Br)	CH_2=$CHCl$	BP; 4 h, 100°	$CHBr_2(CH_2CHCl)_nBr$	1—3	[57]
				(C_1=0.74; C_2=1.77)		
4	$CHCl_2COOCH_3$ (C—H, C—Cl)	CH_2=$CHCH_3$	TBP; 1 h, 150°	$H(CH_2CHCH_3)_n$× ×$CHClCOOCH_3$	1—3	[168]
				$H(CH_2CHCH_3)_n$× ×CCl_2COOCH_3	1—3	
				$Cl(CH_2CHCH_3)_n$× ×CCl_2COOCH_3	1—3	
				$Cl(CH_2CHCH_3)_n$× ×$CHClCOOCH_3$	1—3	[169]
5	CCl_2COOCH_3 (C—Cl)	CH_2=$CHCH_3$	TBP; 1 h, 150°	$Cl(CH_2CHCH_3)_n$ CCl_2COOCH_3 (C_1=2.1; C_2=29.1; C_3=28.2)	1—3	[169]
6	$CCl_2(COOC_2H_5)_2$ (C—Cl)	CH_2=CH_2	BP; 5 h, 100° TBP; 5 h, 130°	$Cl(CH_2CH_2)_n$× ×$CCl(COOC_2H_5)_2$	1—4	[54]
7	FSO_2Cl(S—Cl)	CH_2=CH_2	BP; 25 min, 90°	$FSO_2(CH_2CH_2)_nCl$	1—4	[170]
8	FSO_2Cl(S—Cl)	CH_2=$CHCl$	BP; 45 min, 90°	$FSO_2(CH_2CHCl)_nCl$	1—3	[171]
9	FSO_2Cl(S—Cl)	CH_2=CF_2	BP; 2.5 h, 90°	$FSO_2(CH_2CF_2)_nCl$	1—3	[171]
				$FSO_2CH_2CF_2CF_2CH_2CH_2$× ×$CF_2Cl$	—	

acids by the telomerisation method has been achieved on an industrial scale[160,161].

The VIK acids are highly effective substitutes of dietary and technical plant oils in the paint and varnish industry and other branches of the national economy. Fully oil-free high-quality ML-1121 autoenamels have been devised on their basis at the GIPI LKP, one tonne of VIK replacing up to one tonne of plant oils[162]. Oil-free drying agents have been obtained on an industrial scale on the basis of VIK[161]; the use of VIK makes it possible not only to save up to four tonnes of dietary oils per tonne of VIK but also to increase significantly the activity of the drying agents as a result of the higher concentration of the metal salt and hence their consumption can be reduced.

The VIK and PORK acids are also effective extractants for non-ferrous and rare metals. They make it possible to increase significantly the productivity of extraction processes in hydrometallurgy[163]. The higher fractions of the VIK and PORK acids constitute the basis for the preparation of foam fire extinguishers and de-emulsifying agents[164] and also serve as flotation agents, whereby one can increase by 3—4% the extraction of valuable components from mineral ores, which is extremely important bearing in mind the scale of the mining products processing industry[165]. The main effect of these studies has been the development of a simple technology, the high quality of the telomerisation products obtained, and the possibility of economising on large amounts of dietary and imported technical plant oils.

Table 6. Examples of telomerisation initiated by metal carbonyls.

No.	Telogen (bond dissociated)	Monomer	Initiator and reaction conditions	Identified telomers	n	Refs.
1	CCl_4	CH_2=CH_2	$Mn_2(CO)_{10}$; 2 h, 120°	$CCl_3(CH_2CH_2)_nCl$	1—3	[80]
2	CCl_4	CH_2=CH_2	$Cr(CO)_6$ or $Cr(CO)_5[P(C_6H_5)_3]$; 1 h, 120°	$CCl_3(CH_2CH_2)_nCl$	1—5	[70]
3	CCl_4	CH_2=$CHCH_3$	$Mo(CO)_6$, $W(CO)_6$; 120°	$CCl_3(CH_2CHCH_3)_nCl$	1—3	[69]
4	CCl_4	CH_2=$CHCH_3$	$Cr(CO)_6$*; 1 h, 120-140°	$CCl_3(CH_2CHCH_3)_nCl$	1—3	[71]
5	CCl_4	CH_2=$CHCH_3$	$Fe(CO)_5$, $Cr(CO)_6$; 1 h, 120°	$CCl_3(CH_2CHCH_3)_nCl$	1—3	[72]
6	CCl_4	CH_2=$CClCH_3$	$Fe(CO)_5$ + iso-C_3H_7OH; 4 h, 120°	$CCl_3(CH_2CClCH_3)_nCl$	1—3	[172]
				$CCl_3(CH_2CClCH_3)_2$	—	
7	$CHBr_3$(C—Br)	CH_2=CH_2	$Fe(CO)_5$ + DMF, HMP; 4 h, 100°	$CHBr_2(CH_2CH_2)_nBr$	1—2	[56]
8	$CHBr_3$(C—Br)	CH_2=$CHCl$	$Fe(CO)_5$; 4 h, 80°	$CHBr_2(CH_2CHCl)_nBr$	1—3	[57]
9	$CHBr_3$(C—Br)	CH_2=$CHCl$	$Fe(CO)_5$ + DMF; 4 h, 60°	$CHBr_2(CH_2CHCl)_nBr$	1—2	[57]
10	CH_3CCl_3(C—Cl)	CH_2=CCl_2	$Fe(CO)_5$ + iso-C_3H_7OH; 30 min, 130-140°	$CH_3CCl_2(CH_2CCl_2)_nCl$	1—2	[62]
11	$C_2H_5CCl_3$(C—Cl)	CH_2=$CHCl$	$Fe(CO)_5$ + iso-C_3H_7OH; 3 h, 145°	$C_2H_5CCl_2(CH_2CHCl)_nCl$	1—2	[61]
12	$ClCH_2CH_2CCl_3$(C—Cl)	CH_2=CH_2	$Mn_2(CO)_{10}$ + HMP; 2 h, 120°	$Cl(CH_2)_2CCl_2(CH_2CH_2)_nCl$	1—2	[80]
13	$ClCH_2CH_2CCl_3$(C—Cl, C—H)	CH_2=CCl_2	$Fe(CO)_5$ + HMP; 1 h, 130-135°	$Cl(CH_2)_2CCl_2(CH_2CCl_2)_nCl$	1—2	[62]
				$Cl(CH_2)_2CCl_2(CH_2CCl_2)_nH$	1—2	
				$CCl_3CH_2CHCl(CH_2CCl_2)_nH$	1—2	
14	$ClCH_2CH_2CCl_3$(C—Cl)	CH_2=$CHCOOCH_3$	$Fe(CO)_5$ + DMF; $Fe(CO)_5$ $Mo(CO)_6$, $Mn_2(CO)_{10}$***	$Cl(CH_2)_2CCl_2(CH_2CHCOOCH_3)_nCl$	1—2	[59]
				$Cl(CH_2)_2CCl_2(CH_2CHCHOOCH_3)_nH$	1—2	
15	$C_6H_5CH_2Cl$(C—Cl)	CH_2=CH_2	$Fe(CO)_5$ + HMP, DMF; 4 h, 145°	$C_6H_5CH_2(CH_2CH_2)_nCl$	1—2	[55]
16	$C_6H_5CH_2Cl$	CH_2=$CHCl$	$Fe(CO)_5$ + DMF; 4 h, 145°	$C_6H_5CH_2(CH_2CHCl)_nCl$	1—4	[173]
17	$ClCH_2COOCH_3$(C—H)	CH_2=CH_2	$Mn_2(CO)_{10}$; 2 h, 120°	$H(CH_2CH_2)_nCHClCOOCH_3$	1—3	[81]
				$H(CH_2CH_2)_nC(C_4H_9)ClCOOCH_3$	—	
18	CCl_3COOCH_3(C—Cl)	CH_2=CH_2	$Mn_2(CO)_{10}$, $Mn_2(CO)_{10}$ + DMF; 1 h, 140°	$Cl(CH_2CH_2)_nCCl_2COOCH_3$	1—4	[38]
19	$CCl_3(COOC_2H_5)_2$ (C—Cl)	CH_2=CH_2	$Fe(CO)_5$ + DMF; 5 h, 100-125°	$Cl(CH_2CH_2)_nCCl(COOC_2H_5)_2$	1—2	[54]
20	$CCl_2(COOC_2H_5)_2$(C—Cl)	CH_2=CH_2	$Fe(CO)_5$ + DMF; 4 h, 175°	$Cl(CH_2CH_2)_nCCl(COOC_2H_5)_2$	1—2	[54]
				$CH_3CH_2CClCOOC_2H_5$ | O——CO	—	
				CH_2CH_2 \ C / CO—O | | O—CO / CH_2CH_2	—	
21	FSO_2Cl(S—Cl)	CH_2=$CHCl$	$Fe(CO)_5$ + DMF; 1 h, 90°	$FSO_2(CH_2CHCl)_nCl$	1—4	[170]

* Without co-initiator or in combination with iso-C_3H_7OH, DMF, or HMP (HMP = hexamethylphosphoramide and DMF = dimethylformamide).

** Without co-initiator or in combination with HMP, DMF, or CH_3CN.

*** In combination with cyclohexanol.

As a typical organic reaction, telomerisation gives rise to extensive synthetic possibilities. Tables 5 and 6 present examples of telomerisation, involving halogen-containing telogens and initiators of different kinds, achieved in the Laboratory of Organoelemental Synthesis at the Institute of Organoelemental Compounds of the USSR Academy of Sciences in 1977–1982.

Further study of this productive reaction will undoubtedly lead to the development of its new practical applications.

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Nesmeyanov Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 398 - 430 (1984) U.D.C. 547.221 + 547.288

Fluorine-containing Imines

A.V.Fokin, A.F.Kolomiets, and N.V.Vasil'ev

Data on the methods of synthesis, certain physicochemical properties, and reactivities of fluorine-containing imines of known types are surveyed and the characteristic features of the variation of their properties due to the effects of the fluorine atoms and polyfluoro-substituents at the C = N bond are examined. The theoretical and applied aspects of the development of the chemistry of fluorine-containing compounds with a nitrogen-carbon double bond are discussed.
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I. INTRODUCTION

Imines of different structure, including azomethines (Schiff bases), hydrazones and azines, oximes, carbonylimines (iminoesters, amidines, and chloro- and dichlorocarbonylimines), nitrogen-containing heterocumulenes (isocyanates, isothiocyanates, keten imines, and carbodiimides) as well as substances of other types with a C=N double bond are close to alkenes as regards their importance. Their study is indissolubly linked with the foundation and development of organic chemistry as a science, the development of its methods and theory, particularly the stereochemistry of organic compounds and their reactions, tautomeric phenomena, isomerism, molecular rearrangements, the mechanisms of the stepwise and concerted reactions involving nucleophilic and electrophilic addition to a multiple bond, and cycloaddition reactions.

The applied importance of the chemistry of imines is inestimable. They are precursors or intermediates in the synthesis of many physiologically important substances of biogenic and abiogenic types. Imines are formed as intermediate species in the synthesis of many natural products, monomers for polymerisation, and precursors for other technically important materials. The chemistry of imines can be legitimately regarded as the foundation of the chemistry of heterocyclic compounds, which is vigorously developing and is of great practical importance. The study of the chemistry of imines and iminium salts throws light on processes involved in vital activity associated with the synthesis, metabolism, catabolism, and biocatalytic role of biogenic nitrogen-containing substances.

The first fluorine-containing imines were obtained more than 30 years ago and these compounds have been investigated vigorously during the last two decades. At the same time the extensive data accumulated over a short period on the fluorine-containing imines have made an important contribution to the general chemistry of compounds with a C=N bond.

The interest in fluorine-containing imines is due primarily to practical requirements. The development of components of high-energy fuel compositions, explosives, combustion accelerators, precursors for valuable lubricants and other materials, and intermediates in the synthesis of physiologically important substances constitutes a by no means complete list of problems in the solution of which the chemistry of fluorine-containing imines is involved. During recent years, the interest in the chemistry of fluorine-containing imines increased in connection with the appearance of unique fluorine-containing pesticides and medicinal drugs distinguished by the "suicidal" mechanism of action in relation to pyridoxal enzymes. The intensification of studies of the influence of the imine and iminium groups on the reactions of adjacent fluorine-containing substituents is due to this particular factor.

The available extensive data on fluorine-containing imines cannot be considered in a single article and this is not the aim of the present review. Here an attempt is made to summarise the most important information about fluorine-containing imines and to discover the characteristic features introduced by fluorine atoms of fluorine-containing substituents into various methods for the formation of compounds with an imine group and their properties.

The attainment of the aim formulated proved possible by virtue of the availability of monographs on the chemistry of imines[1-3] and the chemistry of organofluorine compounds[4,5], to which the reader is referred in order to become acquainted with the fundamental problems. It has also been promoted by the existence of data on specific problems in the chemistry of fluorine-containing imines. Thus data on *N*-polyfluoroalkylfluoro- and *N*-polyfluoroalkyldifluoro-carbonylimines (perfluoroaza-alkenes) have been examined by Knunyants and Gontar[6]. The chemistry of *N*-fluoroimino-compounds has been discussed in detail in a book[7], in reviews[8,9], and in an article of a review type[10]. An excellent review[11] deals with the chemistry of fluorine-containing keten imines. The existence of the above publications made it possible to reduce greatly the amount of factual data discussed here, the latter being limited to information in the field of fluorine-containing azomethines which had not been reviewed previously and the most important data on other fluorine-containing imines.

II. METHODS OF SYNTHESIS

Non-fluorinated imines are mainly synthesised by condensing amino-compounds with carbonyl compounds, by eliminating the vicinal substituents at the C–N bond in nitrogen-containing compounds, by the imine exchange reaction, by the condensation of nitroso-compounds with an activated methylene group in various substances, and also by the oxidation of secondary amines and their derivatives. The first method is the most general. Many specific methods for the synthesis of imines are also known. These include procedures based on the cleavage of unsaturated compounds by primary amines, on cycloaddition–decomposition reactions, on the isomeric transformations of unsaturated nitrogen-containing compounds, on the functional transformation of

compounds with an imine group, etc. Almost all these methods have been tested in the synthesis of fluorine-containing imines but by no means all proved suitable for this purpose.

It is believed[1] that the condensation of amines with non-fluorinated carbonyl compounds proceeds as a reversible process:

$$>C=O + H_2NR \rightleftarrows \left[>C\begin{matrix}OH\\NHR\end{matrix} \right] \rightleftarrows >C=NR \quad .$$

In neutral media the rate-limiting stage is the formation of the addition product—the corresponding hemiaminal. However, fluorine-containing carbonyl compounds, especially perfluoroketones, are such powerful electrophiles that they interact vigorously not only with amines, hydrazines, and hydroxylamines but also with weak nucleophiles such as acid amides and sulphonamides[12-23], forming stable geminal aminohydroxy-compounds:

$$R_FR_F'C=O + H_2NR \rightarrow R_FR_F'C\begin{matrix}OH\\NHR\end{matrix} \quad ;$$

$$R = H, Alk, Ar, OH, NR_2, C(O)R, SO_2R \quad .$$

The synthesis of fluorine-containing imines is therefore not limited by the first stage except for amino-compounds whose basicity is extremely low and which are sterically hindered[24,25]. In most cases the second stage of the reaction—the dehydration of the geminal aminohydroxy-compound formed—is rate-limiting.

As a result of the above feature, by no means all fluorine-containing imines can be obtained by the condensation of fluorocarbonyl compounds with amino-compounds, by analogy with the corresponding hydrocarbon compounds. Under the usual conditions in the absence of a catalyst or in the presence of weak dehydrating agents (inorganic and carboxylic acids), only the imines of partly fluorinated carbonyl compounds are formed, for example, the anils of trifluoroacetone[17,26,27], the anil of trifluoroacetophenone[28], the imines of aromatic polyfluoro-substituted ketones and aldehydes[29-33], and the hydrazones of partly fluorinated ketones[34-36]. Fluorine-containing aldimines are readily formed under the usual conditions; instead of polyfluoroaldehydes, it is possible to employ in this instance their hydrates and other derivatives[37-41].

Among the imines of highly electrophilic perfluoroketones, only the hydrazones have been obtained by the condensation of the polyfluoroketones with hydrazines in trifluoroacetic acid[42,43]. Other types of perfluoroketone imines are not formed under the usual conditions in view of the stabilisation of the C–O bond in geminal aminohydroxy-compounds by perfluoroalkyl and especially trifluoromethyl groups[12-18]. The stabilisation effects are so marked that the thermolysis of the adducts obtained by the addition of perfluoroketones to amino-compounds does not lead to their dehydration but results in various destructive transformations, which lead to the formation of either the starting materials[17,18,20,24-26], or the products of their oxidation-reduction reactions[15,44,45], or the products of the "haloform" decomposition[8,36,46-49].

The adducts of amino-compounds with asymmetric polyfluoroketones frequently undergo the "haloform" decomposition even under mild conditions[36,47]:

$$R_FR_F'C=O + H_2NR \rightarrow R_FC(O)NHR + HR_F' \quad .$$

These reactions can be sometimes prevented by regulating the pH of the medium. Thus the phenylhydrazone and the oxime of difluoronitromethyl methyl ketone, which is highly sensitive to bases, are formed only in a neutral medium[48,49].

The stability of the adducts of perfluoroketones with amino-compounds is reduced and the tendency towards decomposition into the initial reactants increases with decrease of the basicity of the amino-compounds employed[17,18,24-26,50-52]. Thus the hemiaminals of hexafluoroacetone are stable substances which can be distilled without decomposition. On the other hand, the hemiamidals of hexafluoroacetone, obtained from carboxylic acid amines, are stable up to 100 °C [20,52] and those obtained from perfluorocarboxylic acid amides are stable only up to 50 °C:[24] the adducts of hexafluoroacetone with the amides of perfluorodicarboxylic acids are stable at atmospheric pressure only in solutions in the presence of an excess of hexafluoroacetone and at a temperature below 0 °C.[25] Thus the properties of the adducts of amino-compounds with polyfluoroketones vary within extremely wide limits, which must hinder the development of a general method for their conversion into fluorine-containing imines.

At the same time, under the conditions of concerted reactions, almost all the fluorine-containing geminal aminohydroxy-compounds could be involved in reactions involving dehydration by mild dehydrating agents. Thus various imines[19], hydrazones, and azines of polyfluoroketones[53], *N,N'*-bis(hexafluoroisopropylidene)diamides of perfluorodicarboxylic acids[25], and *N*-hexafluoroisopropylideneamidines[54] have been obtained by dehydration with $POCl_3$ in pyridine. Hexafluoroacetone azine[55] and the perfluoroacylimines of hexafluoroacetone[24] have been synthesised with the aid of $POCl_3$ in quinoline. Trifluoroacetic acid anhydride in pyridine or quinoline proved to be effective in the synthesis of the acylimines of perfluoroketones[56] and the phosphoryl- and sulphonyl-imines of hexafluoroacetone[57,58]:

$$R_FR_F'C=O + H_2NR \rightarrow R_FR_F'C\begin{matrix}OH\\NHR\end{matrix} \xrightarrow{-H_2O} R_FR_F'C=NR \quad ;$$

$$R = H, Alk, Ar, NH_2, NR_2, N=CR_2, C(O)R, C(O)R_F, P(OR)_2, S(O)Ar \quad .$$

Other dehydrating agents also proved to be effective. Thus thionyl chloride converts smoothly and almost quantitatively the adducts of polyfluoroketones and sulphonamides into the corresponding sulphonylimines[21,22]. Asymmetric fluorine-containing azines have been obtained by heating the adducts with P_2O_5.[59,60] Oleum has been used successfully to synthesise the perfluoroacylimines and the azine of hexafluoroacetone[50,61]. Pentafluoro-2-azopropene in the presence of KF proved to be an effective dehydrating agent in the synthesis of hexafluoroacetone acylimines[62]:

$$R_FR_F'C=O \xrightarrow{H_2NSO_2R} R_FR_F'C\begin{matrix}OH\\NHSO_2R\end{matrix} \xrightarrow{SOCl_2} R_FR_F'C=NSO_2R \quad ;$$

$$R_F, R_F' = CF_3, ClCF_2, O_2NCF_2; \; R = Me, Ph, 4\text{-}MeC_6H_4 \quad ;$$

$$(CF_3)_2C=NNH_2 + O=CRR' \xrightarrow{P_2O_5} (CF_3)_2C=N-N=CRR' \quad ;$$

$$R, R' = Alk, Ar$$

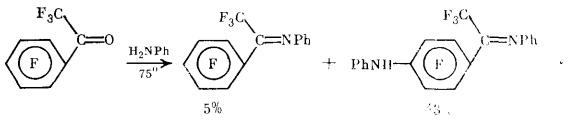
$$(CF_3)_2CNHC(O)R \xrightarrow{SO_3} (CF_3)_2C=NC(O)R \xleftarrow[-CF_3NCO,\,-HF]{CF_3N=CF_2} (CF_3)_2CNHC(O)R' \quad ;$$

$$R = CF_3, C_4F_9; \; R' = Me, Et, Ar \quad .$$

The use of mild dehydrating agents made it possible to extend greatly the assortment of imines obtained by the reactions of polyfluoroketones with amino-compounds. The considerable prospects for the further improvement and development of this method are now quite evident.

The preparative value of the condensation of polyfluoroketones with various amino-compounds in the presence of dehydrating agents is not limited to the synthesis of fluorine-containing imines and is acquiring increasing importance as a method of synthesis of a wide variety of fluorine- and

nitrogen-containing heterocycles[34,39,51,54,60,63-71]. They are formed on dehydration of the adducts of polyfluoroketones with amino-compounds containing functional groups such as OH, SH, NH_2, COOH, C≡N, etc. in the α-, β-, or γ-position relative to the NH_2 group. It is noteworthy that, when these reactions are carried out in highly electron-donating protophilic media, it is possible to eliminate the use of dehydrating agents, using instead an excess of the highly electrophilic polyfluoroketone[65-68]. In conclusion of the discussion of the reactions of polyfluoroketones with amino-compounds, we may mention one of the features of the condensation of perfluoroaryl ketones with amines associated with the ability of the fluorine atom in the perfluoroaryl group to undergo readily nucleophilic substitution which results in the formation of an amino-derivative[30,31]:



This process was facilitated by carrying out the condensation in the presence of $AlCl_3$ or H_2SO_4,[30,31] which led to simple and selective methods of synthesis of polyfluorinated Schiff bases (see the review of Gerasimova and Fokin[72]).

The imine exchange reactions, which are widely used in the syntheses of imines of the hydrocarbon series, proved suitable also for the preparation of certain fluorine-containing imines. The characteristic features of this method are the high stability of the fluorine-containing aminals and aminoketals, which like the geminal aminohydroxy-compounds, are frequently isolated in a pure state[17-20,25,56,58,59,71]. The transamination of fluorine-containing imines is therefore carried out as a severe thermal process[17-20] and the imine exchange takes place at room temperature only in the presence of amine acceptors[17,26,59]:

$$R_F^1R_F^2C{=}NR \xrightarrow{H_2NR'} R_F^1R_F^2C\begin{matrix}NHR\\NHR'\end{matrix} \xrightarrow{\Delta(H^+)} R_F^1R_F^2C{=}NR' .$$

The characteristic features of these reactions have not so far been studied in detail. It has only been shown that hexafluoroacetone imines can be used for the selective synthesis of the corresponding oximes and hydrazones. The acyl- and sulphonyl-imines of hexafluoroacetone can probably be regarded as precursors of the corresponding anils.

Certain side reactions accompanying the transamination of fluorine-containing imines are known. The imines of asymmetric polyfluoroketones undergo the haloform decomposition in these reactions[17]. In a number of cases reactions in which fluorine- and nitrogen-containing heterocyclic compounds are formed take place instead of the imine exchange.

The transformations of fluorine-containing geminal aminohydroxy-compounds and aminals into the corresponding imines can also be regarded as processes involving the elimination of vicinal substituents at the C–N bond in saturated fluorine- and nitrogen-containing compounds. Similar reactions (dehydrofluorination and reductive dehalogenation) are used widely in the syntheses of *N*-fluoroimines (see the review of Fokin et al.[8]). Thermal transformations of amino- and amido-ketals of polyfluoroketones in the presence of phosphorus pentoxide also lead to fluorine-containing imines[18,37,73]:

$$F_3C\begin{matrix}OR''\\NHR'\end{matrix}R \xrightarrow{\Delta,\ P_2O_5} F_3C{=}NR' ;$$

R = H, CF_3; R' = NHC(O)NH_2, C(O)R_F, $SO_2C_6H_4CH_3$-*p* .

Cycloaddition–decomposition reactions have found extensive applications in the syntheses of fluorine-containing imines. This procedure proved to be one of the convenient methods for the preparation of difluorocarbonylimines[8], fluorine-containing keten imines, including compounds with perfluoroalkyl groups at the nitrogen atom[11], and also various fluorine-containing azomethines and acylimines of polyfluoroketones[15,17,20,26]. In many cases this method makes it possible to obtain imines which cannot be synthesised by other procedures. Thus the extension of the Staudinger reaction to fluorine-containing carbonyl compounds permitted the synthesis even of the imines of asymmetric ketones which undergo the "haloform" decomposition in other syntheses:

$$F_3C(R)C{=}O + Ph_3P{=}NR' \xrightarrow[-Ph_3PO]{\Delta} F_3C(R)C{=}NR' ;$$

R = Me, CF_3, O_2NCF_2; R' = H, Ph, C(O)Me, C(O)Ph, C(O)OEt .

Decomposition with formation of difluoronitromethane and trifluoroacetyliminotriphenylphosphorane has been noted only in the reaction of triphenylphosphine imine with nitroperfluoroacetone[26].

A modification of the Staudinger reaction, in which isocyanates and catalytic amounts of triphenylphosphines oxide[26,74] or dimethylformamide[75] are used instead of iminophosphoranes, is extremely interesting:

$$O{=}C{=}NR \xrightarrow[150-180^\circ]{X=O} \left[\vphantom{\frac{1}{1}}\right. \text{cyclic intermediate} \xrightarrow[-CO_2]{} X{=}NR \left.\vphantom{\frac{1}{1}}\right] \xrightarrow[-X=O]{(CF_3)_2C=O} (CF_3)_2C{=}NR ;$$

X = Ph_3P, R = Ar; X = $(CH_3)_2NCH$, R = C_6F_5 .

In the absence of catalysts, this reaction does not take place even under much more severe conditions.

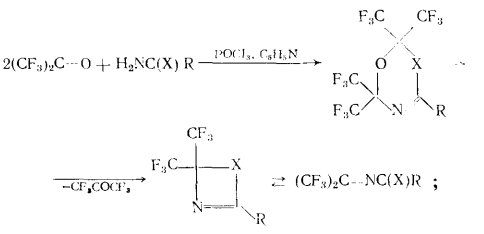
The interaction of hexafluoroacetone with thionylimines in the presence of CsF [76] and the thermal reactions of octafluoroisobutene with nitrosobenzene[77] are apparently processes of the cycloaddition–decomposition type:

$$(CF_3)_2C{=}O \xrightarrow[-SO_2]{O{=}S{=}NAr} (CF_3)_2C{=}NAr \xleftarrow[-COF_2]{ON-Ph} (CF_3)_2C{-}CF_2 .$$

Many cyclodecomposition reactions, leading to fluorine-containing imines, have no analogues in the hydrocarbon series. Thus the nucleophilic cleavage of tetrakis(trifluoromethyl)-1,3-dithietan by amino-compounds leads to various hexafluoroacetone imines[78]. The yield of the reaction products is higher the lower the basicity of the amino-compound:

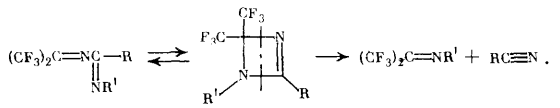
$$(CF_3)_2C\begin{matrix}S\\S\end{matrix}C(CF_3)_2 \xrightarrow{H_2N-R} (CF_3)_2C{=}NR .$$

2,2,6,6-Tetrakis(trifluoromethyl)-1,3,5-oxathiazines and the corresponding 1,3,5-oxadiazines are effective precursors of hexafluoroacetone thioacylamines[63,79-82] and hexafluoroisopropylideneamidines[54,83]. Thermolysis with elimination of hexafluoroacetone leads in these cases to the derivatives of 1,3-thiazete and 1,3-diazete, which are converted into imines under certain conditions:

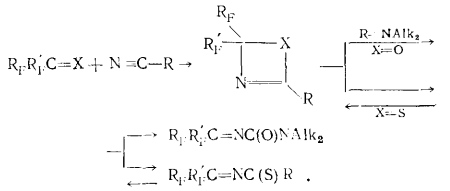


Derivatives of 1,3-thiazete proved to be extremely stable, undergoing electrocyclic reactions only on heating to 150 °C.[79] On the other hand, derivatives of 1,3-diazete

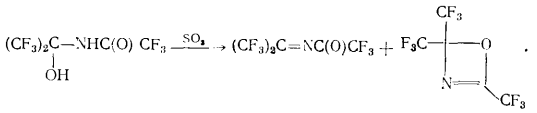
readily isomerise under the usual conditions to amidines and the presence of these compounds in the equilibrium mixture has been confirmed by the isolation of the products of their retro-[2 + 2]-cycloaddition[54]:



The formation of fluorine-containing 1,3-oxazetes and 1,3-thiazetes in [2 + 2]-cycloaddition reactions of polyfluoroacetones and hexafluorothioacetone with acid nitriles has been demonstrated recently[84]. In contrast to derivatives of 1,3-thiazete and 1,3-diazete, 1,3-oxazetes isomerise reversibly to acylimines:

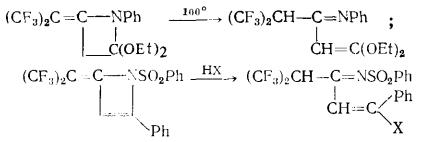


It is noteworthy that the dehydration of the adduct of hexafluoroacetone and trifluoroacetamide by sulphur trioxide also leads to a four-membered unsaturated heterocycle—2,2,4-tris(trifluoromethyl)-1,3-oxazete, which was isolated in the form of a complex with SO_3.[50] The oxazete stabilised by three trifluoromethyl groups does not change at 150 °C and undergoes irreversible ring opening only in the presence of bases:

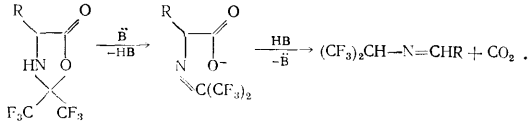


This indicates a concerted mechanism of the condensation of polyfluoroketones with acid amides in the presence of dehydrating agents and one may expect that, under certain conditions, the products of these reactions may be exclusively 1,3-oxazates.

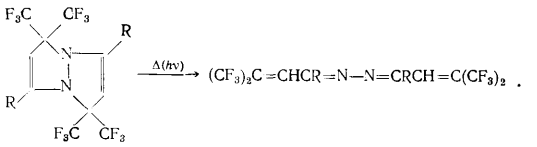
Among other electrocyclic reactions leading to fluorine-containing imines, mention should be made of the transformations of cyclic [2 + 2]-adducts of fluorine-containing keten imines with a ketenal or with acetylenes, ring opening being accompanied by a proton shift[85,86]:



The anionotropic cyclodecomposition with formation of fluorine-containing imines in the catalysed reactions of 2,2-bis(trifluoromethyl)-1,3-oxazolidin-5-ones is of interest[87]:

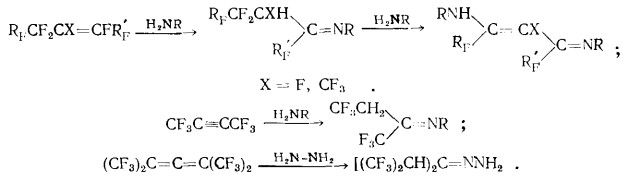


The formation of symmetrical fluorine-containing azines in high yields in the thermal or photolytic decomposition of the adducts of hexafluoroacetone azine with acetylenes is likewise striking[88]:

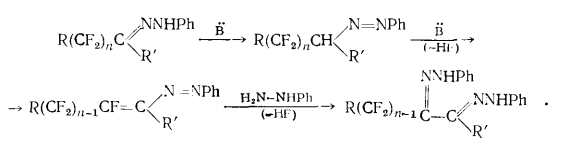


The electrocyclic reactions described are distinguished by high selectivity, so that the formation of fluorine-containing imines in various heterocyclic reactions of fluorine- and nitrogen-containing compounds constitutes a kinetically and thermodynamically most favourable process.

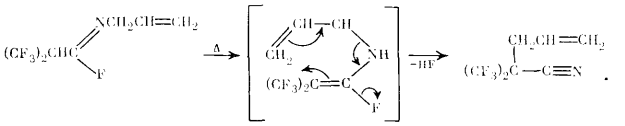
Many methods of synthesis characteristic of fluorine-containing imines alone are based on the reactions of amino-compounds with polyfluoroalkenes. Terminal polyperfluoroalkenes are converted in these reactions into imidoyl fluorides, which are intermediates in the synthesis of keten imines[11], and into hydroxamoyl fluorides, amidines, hydrazidines, etc.[5]. The analogous reactions of amino-compounds with inner perfluoroalkenes, perfluorocycloalkenes, alkynes, and allenes initially lead in all cases to α-hydropolyfluoroketone imines[89–91] and, under conditions suitable for dehydrofluorination, the imines formed undergo further reactions with formation of iminoenamines[92–99], iminonitriles[91], and iminoketen imines[100], for example:



The characteristics of these reactions specified above show that prototropic shifts from C to N in CCN triad systems are less characteristic of fluorine-containing imines than of the imines of non-fluorinated carboxylic ketoacids. Triad prototropism of the enamine–imine and enehydrazine–hydrazone type therefore takes place extremely rapidly and the equilibrium is fully displaced to compounds with a C=N bond. However, the azo–hydrazone prototropism is achieved relatively easily, which has been manifested by the mild conditions in the conversion of fluorine-containing hydrazones into polyhydrazones[34,38–40,43,101]:



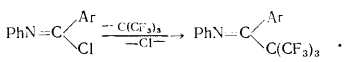
The conditions governing the thermal 1,3-sigmatropic transformations of *N*-allyl-2*H*-hexafluoroisobutyroimidoyl fluoride[102], which can be achieved only under the conditions of the C → N proton shift, may serve as a qualitative characteristic of the tendency of fluorine-containing imines to undergo triad prototropism of the imine–enamine type:



Since the "aza-Claisen" rearrangement of the compound takes place on heating above 120 °C, the energy barrier to the process must be estimated as more than 15 kcal mol^{-1}.

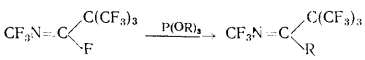
A large number of special methods for the synthesis of fluorine-containing imines, based on the anionotropic and free radical reactions of fluorine- and nitrogen-containing compounds, on cycloaddition reactions, etc., have been described.

Nonafluoro-t-butylpotassium readily reacts with chlorocarbonylimines to form products of the nucleophilic substitution of the chlorine atom[103]:



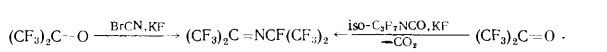
These reactions resemble the reactions of chlorocarbonylimines with organometallic compounds widely investigated in hydrocarbon chemistry.

The alkylation of certain fluorocarbonylimines has been achieved with the aid of trialkyl phosphites[104]:

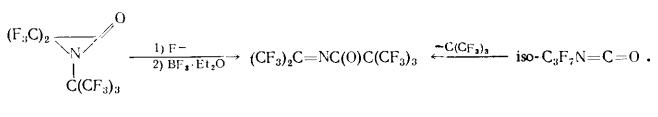


Fluorophosphoranes are apparently intermediates in this case.

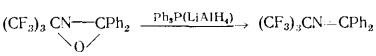
Hexafluoroacetone perfluoroisopropylimine is formed on reaction of hexafluoroacetone with bromocyanogen or perfluoroisopropyl isocyanate in the presence of potassium fluoride[105]:



The reaction of nonafluoro-t-butylcaesium with perfluoroisopropyl isocyanate led to hexafluoroacetone nonafluoropivaloylimine[106]. An elegant synthesis of this compound has also been achieved by the nucleophilic opening of the ring of the corresponding perfluoro-α-lactam by the fluoride ion:

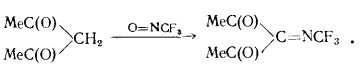


Benzophenone perfluoro-t-butylimine has been obtained by the nucleophilic deoxygenation of the corresponding oxaziridine[107]:

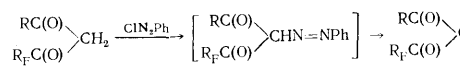


Analogous syntheses are also known for non-fluorinated imines.

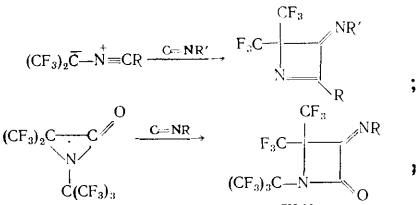
In the presence of bases, trifluoronitrosomethane reacts with acetylacetone, which made it possible to obtain diacetyl ketone trifluoromethylimine[108]:

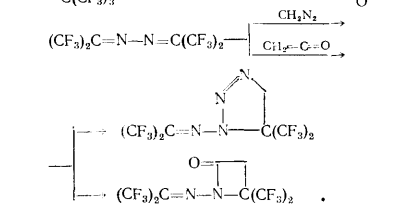


This reaction can be regarded as an analogue of the condensation of nitroso-compounds via the activated methylene group of strong CH acids (the Ehrlich–Sachs reacton), which has been widely investigated in hydrocarbon chemistry. Like non-fluorinated β-diketones, fluorine-containing β-diketones react with benzenediazonium chloride[34,70]:



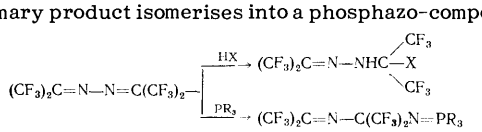
The [3 + 1]-,[81,109–113] [2 + 2]-,[86,114] and [2 + 3]-cycloaddition[115] reactions have been used successfully for the synthesis of cyclic fluorine-containing imines:



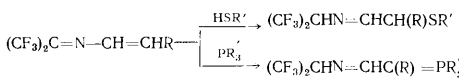


The trimerisation of fluorine-containing 1,3-diazadienes with a terminal methylene group also leads to similar compounds[54].

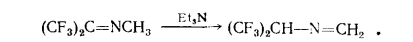
Selective reactions of fluorine-containing imines made it possible to achieve the synthesis of a large number of the compounds under consideration via functional transformations with retention of the C=N bond. For example, hexafluoroacetone azine combines smoothly with nucleophiles via one of the C=N bonds and is converted into hydrazones, while on interaction with trialkyl phosphites or tertiary phosphines the primary product isomerises into a phosphazo-compound[115–117]:



Hexafluoroacetone alkenylimines interact with nucleophiles via the 1,4-addition mechanism[118,119]:

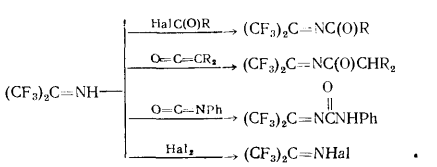


In contrast to their non-fluorinated analogues, hexafluoroacetone alkylimines undergo the imine–imine prototropic shifts extremely readily even in the presence of triethylamine[120]:

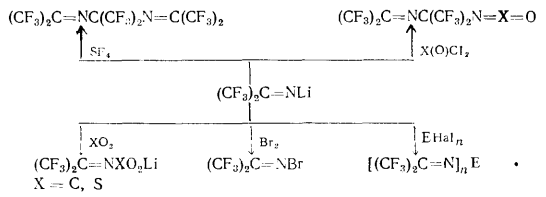


In the hydrocarbon chemistry such reactions take place at a low rate only in the presence of extremely strong bases.

Hexafluoroacetone imine and hydrazone are precursors of a large number of fluorine-containing imines. They have been involved in acylation by acyl halides[60], ketens[19,73,121], and isocyanates[17,60]; the substitutional halogenation of hexafluoroacetone imine has been achieved in the presence of alkali metal fluorides[122]:



Hexafluoroacetone *N*-lithioimine proved to be more reactive in reactions with various electrophiles. On intense cooling. this compound is smoothly brominated[19], forms addition products with sulphur dioxide or carbon dioxide[123], forms substitution products on reaction with chlorotrimethylsilane, phosphorus trichloride, arsenic trichloride, sulphur dichloride, boron halides, sulphene chlorides, and sulphinyl chlorides[124], and sulphur tetrafluoride[125]:



Instances of the conversion of fluorine-containing oximes into imines are known. For example, hexafluoroacetone dichlorophosphorylimine has been obtained by the reaction of hexafluoroacetone oxime nitrite with phosphorus trichloride[126]:

$$(CF_3)_2C{=}NONO \xrightarrow{PCl_3} (CF_3)_2C{=}NP(O)Cl_2 \ .$$

Reactions involving the fluorination of amines, amides, imines, iminoesters, amidines, and guanidine and its derivatives by elemental fluorine as well as the reactions of unsaturated compounds with tetrafluorohydrazine, chlorodifluoroamine, and difluoroamine are widely used in the synthesis of *N*-fluoroimines with a fluorinated hydrocarbon group. In combination with the dehydrofluorination, reductive dehalogenation, and homolytic decomposition reactions of the substances formed, the above processes made it possible to devise a large number of specific methods for the synthesis of *N*-fluoroimines of different structure, which have been examined in detail in a number of communications[8-10, 127-129].

The reactions of electrophiles with nitriles have been used recently for the synthesis of *N*-halogenoimines. For example, halogenofluorosulphates react with the nitriles of perfluorocarboxylic acids under mild conditions[130]; on heating in the presence of a strong inorganic acid, polyfluoroalkyl hypochlorites add to nitriles[131]:

$$R_F{-}C{\equiv}N + HalOSO_2F \rightarrow R_F{-}C\!\!<\!\!\begin{matrix}NHal\\OSO_2F\end{matrix} \ ;$$

$$R_F{=}CF_3,\ NO_2CF_2,\ (NO_2)_2CF,\ n\text{-}C_3F_7 \ .$$

$$R_F{-}C{\equiv}N + ClOCH_2(CF_2)_4H \xrightarrow[110\text{-}115^\circ]{H^+} R_F{-}C\!\!<\!\!\begin{matrix}NCl\\OCH_2(CF_2)_4H\end{matrix} \ .$$

There are comparatively few data on homolytic reactions leading to fluorine-containing imines. At the same time the possibility, in principle, of employing for these purposes reactions based on the properties of carbenes and carbenoid species as well as the high tendency of the N–Hal bonds in halogenoimines towards homolysis have been demonstrated; the prospects of the synthesis of fluorine-containing imines via the pyrolytic reactions of fluorine- and nitrogen-containing unsaturated compounds have been assessed.

Thus bis(trifluoromethyl)diazomethane alkylates hexafluoroacetone imine fairly smoothly[132] and its pyrolysis in the presence of alkanes leads to hexafluoroacetone hydrazones[133] in a mixture with other substances:

$$(CF_3)_2CN_2 \begin{cases} \xrightarrow{HN{=}C(CF_3)_2} (CF_3)_2CHN{=}C(CF_3)_2 \\ \xrightarrow{\Delta,HR} (CF_3)_2C{=}NNHR \end{cases} .$$

Thermal reactions of bis(trifluoromethyl)diazirine lead to hexafluoroacetone azine[134], while heating in the presence of alkanes results in the formation of hexafluoroacetone alkylimines[133]:

$$(CF_3)_2C\!\!<\!\!\begin{matrix}N\\N\end{matrix} \begin{cases} \xrightarrow{\Delta} (CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \\ \xrightarrow{HR,165^\circ} (CF_3)_2C{=}NR \end{cases} .$$

Isonitriles react smoothly with perfluoroalkyl iodides to form fluorine-containing iodocarbonylimines[135]:

$$RN{=}C + IR_F \rightarrow RN{=}C\!\!<\!\!\begin{matrix}R_F\\I\end{matrix} \ .$$

Many cyclic fluorine-containing imines have been obtained in reactions involving [1 + 4]-cycloaddition of isonitriles to fluorine-containing unsaturated compounds (see below).

It has been shown that *N*-halogenoimines are converted under the conditions of photolysis into the corresponding azines[19]; in the presence of metallic mercury, these compounds readily condense with sulphene chlorides and acyl chlorides[136]:

$$(CF_3)_2C{=}NHal \begin{cases} \xrightarrow[Hal=Br]{h\nu} (CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \\ \xrightarrow[Hg]{HalX} (CF_3)_2C{=}NX \end{cases} ;$$

$$X = SCF_3,\ C(O)CF_3 \ .$$

The pyrolysis of hexafluoroacetone azine with alkanes or alkenes[137,138] leads to mixtures of substances containing hexafluoroacetone hydrazones:

$$(CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \begin{cases} \xrightarrow{(CH_3)_2C{=}C(CH_3)_2} \\ \xrightarrow{HR} \begin{cases} \rightarrow (CF_3)_2C{=}NNHC(CF_3)_2CH_2C(CH_3)_2 \\ \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\qquad\quad CH_3 \\ \rightarrow (CF_3)_2C{=}NNHC(CF_3)_2R \end{cases} \end{cases} .$$

When hexafluoroisopropylideneiminoxybis(trifluoromethyl)amine was heated with polyfluoroethylenes, the products of the insertion of an alkene in both N–O bonds were obtained[139]:

$$(CF_3)_2C{=}NON(CF_3)_2 \xrightarrow{CF_2{=}CFX} (CF_3)_2C{=}NCF_2CFXON(CF_3)_2 +$$

$$+ (CF_3)_2C{=}NOCF_2CFXN(CF_3)_2 \ ;$$

$$X = F,\ Cl \ .$$

The above data indicate the extremely wide variety of the methods of synthesis of polyfluorinated imines. They are formed as a result of anionotropic, cationotropic, and homolytic reactions, concerted and stepwise electrocyclic processes, and cycloaddition–decomposition reactions.

The formation of extremely stable intermediates, which are converted into the final imines as a result of severe stepwise or mild concerted processes, is characteristic of the majority of the methods. As fluorine atoms of polyfluoroalkyl groups accumulate at the C=N bond of the intermediate, the efficiency of the stepwise processes falls and that of the concerted processes increases. This apparently reflects a common feature of fluorine-containing imines—a marked increase of strain in the latter with increase of the number of fluorine atoms and polyfluoroalkyl groups at the C=N bond.

III. CERTAIN PHYSICOCHEMICAL PROPERTIES

The physicochemical properties of fluorine-containing imines have been little investigated. A broad set of characteristics has been established only for isolated compounds among *N*-fluoromines of practical importance[8]. For the remaining compounds, the boiling points and in certain cases the refractive indices and densities are known. The majority of the fluorine-containing imines have been characterised by their infrared spectra [ν(C=N)] and their ^{19}F and ^{1}H NMR spectra. The thermodynamic parameters have been determined only for certain *N*-fluoroimines; in a number of instances the geometrical parameters of the molecules of these compounds have been calculated[8].

The characteristics of the physicochemical properties of the compounds considered have been expressed most strikingly in the series of perfluoroketone imines whose parameters are partly compiled in the Table. It follows from the data presented that, in contrast to their hydrocarbon analogues,

fluorine-containing imines are relatively low-boiling liquids, while certain perfluoroimines are gases under the usual conditions. Low boiling points are characteristic even of amines with mobile hydrogen atoms in the molecule, which indicate extremely weak forces of dipole–dipole interactions, a low energy of the intermolecular $n\pi$ interactions, and a weak hydrogen bond between the molecules of fluorine-containing imines in the liquid state. These findings are correlated with the sharp decrease of the basicity and the "amphoteric" properties of the imine after the introduction of fluorine atoms or polyfluoroalkyl groups at the C=N bond.

The boiling points and spectroscopic parameters of the imines $(CF_3)_2C{=}N{-}R$.[19,59,74,122,140]

R	B.p., °C	ν(C = N), cm^{-1}	$\delta[(CF_3)_2C=N]$, p.p.m.*	
			syn-	*anti-*
H	16—16.5	1670	—2.9	—1.1
F	—10—-8	1620	—12.9	—9.7
Cl	—	1630	—9.0	—7.4
Br	49.5—50	1650	—6.6	—5.6
OH	72—73	—	—10.9	—8.8
OCH_3	—	—	—11.4	—9.2
NH_2	95.5—96.0	1600	—13.4	—12.0
NHC_6H_5	—	1664	—15.8	—8.7
$N(CH_3)_2$	—	—	—24.4	—12.7
$N{=}C(CF_3)_2$	67—67.5	1660	—11.5	—7.8
CH_3	34—35	1705	—11.3	—5.2
C_6H_5	135—137	1680	—16.6	—8.6
iso-C_3F_7	—	1750	—11.6	—5.2
SCF_3	51.3	1655	—	
$Si(CH_3)_3$	84.7	1770	—	
$C(O)CH_3$	85	1735	—5.7	
$C(O)CF_3$	45	1750	—8.1	
$S(O)CF_3$	86.7	1675	—	
$S(O)C_6H_5$	41(0.05 mm)	1600	—13.2	
$SO_2C_6H_5$	100(5.0 mm)	1750	—3.9	

*Relative to CF_3COOH.

It is noteworthy that the reduced basicity and weak "amphoteric" properties of fluorine-containing imines are responsible for their increased stability and their much smaller tendency towards oligomeric transformations than for the non-fluorinated analogues. This is the reason for the existence under the usual conditions of the fluorine-containing analogues of many aliphatic imines of the hydrocarbon series, which are unknown in their free state.

The high volatility of perfluoroketone hydrazones and especially their oximes, which are fairly strong acids, must be regarded as extremely interesting[141]. This can be explained by the weak *s* character of the hybrid state of the orbitals not only of the *p* electrons of the imine nitrogen but also of the *p* electrons of the heteroatom linked to the imino-group, which is possible only in the presence of additional many-centre molecular orbitals in the CNO and CNN triads of fluorine-containing imines. Data indicating the extremely high stability and the relative ease of formation of the oximes and hydrazones of fluorocarbonyl compounds compared with fluorine-containing azomethines are consistent with this finding.

The analysis of the vibrational spectra of fluorine-containing imines leads to a similar conclusion. Judging from these characteristics, the imine bond in the compounds considered is more sensitive to various effects of substituents than in the molecules of the hydrocarbon analogues. Thus the stretching vibration frequencies of the C=N bond in fluorine-containing imines are manifested in the region from 1770 cm^{-1} for hexafluoroacetone trimethylsilylimine (see Table) to 1553 cm^{-1} for the *N*-fluoroimine of the dinitrile of mesoxalic acid[8]. The corresponding range for the imines of the hydrocarbon series is from 1680 to 1600 cm^{-1}.[1] Even for the monosubstituted hexafluoroacetone anils, the stretching vibration frequency of the C=N bond varies from 1698 to 1592 cm^{-1} depending on the nature and position of the substituent in the benzene ring[140].

When the dependence of the vibrational spectra of fluorine-containing imines on structure is considered (see Table), it is striking that only in the presence of a pair of *p* electrons in the substituent at the imine nitrogen (*N*-halogenomines, oximes, hydrazones, azines, sulphenylimines, and sulphinylimines) are the vibrations of the C=N bond manifested in the region characteristic of the hydrocarbon analogues and the degree of displacement of this band towards lower energies is correlated with the increase of the overlap integral of the orbitals of the valence electrons of the imine nitrogen and the substituent. In the absence of substituents with a pair of *p* electrons, the energy of the stretching vibrations of the C=N bond of the fluorine-containing imine is much higher than in the hydrocarbon analogues and increases with enhancement of the electron withdrawing effects of the substituent at the imine nitrogen.

The dependence of the ^{19}F NMR spectra of hexafluoroacetone imines on structure is unusual (see Table). Substituents at the imine nitrogen having *p* electrons diminish the shielding of the fluorine nuclei of the CF_3 group in parallel with the increase of the overlap integral of the orbitals of the imine nitrogen and the substituent of this type. Analogous effects are introduced by other substituents of the *+E* type, which has been shown particularly clearly in the series of hexafluoroacetone anils[140] and in this case too a shift of the stretching vibration bands of the C=N bond towards lower energies has been observed simultaneously with diminution of the shielding of the fluorine nuclei. Such a complex dependence is possible only for the "acetylenic" type of π overlap via the C=N bond in the compounds considered, which is fully consistent with their enhanced electrophilic properties.

Additional information about the compounds considered is provided by the results of the study for the dynamics of the ^{19}F NMR spectra[142]. Two groups of signals due to non-equivalent polyfluoroalkyl groups usually appear in the spectra of imines of fluorine-containing symmetrical ketones having a fairly rigid C=N bond [14,19,59,122,140]. The study of the temperature variation of the spectra makes it possible to discover the energy barrier to the *Z*/*E* transition[14,59,74,143], which consitutes a quantitative measure of the rigidity of the imine linkage.

The energy barriers of the *Z*/*E* transitions ($\Delta G''$) have now been estimated for *N*-perfluoroisopropyldifluorocarbonylimine[1] (approximately 11 kcal mol^{-1}), hexafluoroacetone perfluoroisopropylimine[14] (13.4 kcal mol^{-1}), and hexafluoroacetone anils[74] (14.35–15.45 kcal mol^{-1}). According to the results of Dowson et al.[143], $\Delta G''$ for aliphatic hexafluoroacetone imines varies from 12.0 to 20.5 kcal mol^{-1} depending on the degree of branching of the alkyl group. Presumably the rigidity of the C=N bond in these compounds is determined by the hyperconjugation of the alkyl substituent. Thus hexafluoroacetone methylimine is distinguished by the maximum energy barrier to *Z*/*E* isomerisation (20.5 kcal mol^{-1}). For compounds with a secondary alkyl group (isopropyl and α-hydrohexafluoroisopropyl), the $\Delta G''$ are 17.5 and 18.5 kcal mol^{-1} respectively, while the values for compounds with a "tertiary" alkyl group (t-butyl, perfluoroisopropyl, and α-chlorohexafluoroisopropyl) are 12.0–13.7 kcal mol^{-1}.

Thus the C=N bond in perfluoroketone imines is much less rigid than in the imines of the hydrocarbon series, where the $\Delta G''$ are greater than 25 kcal mol^{-1} even for aliphatic

representatives[1,142]. The greatest increase of the rigidity of the imine bond in the compounds considered is apparently attained as a result of hyperconjugation effects; the barrier to the *Z*/*E* isomerisation of perfluoroketone imines is increased by substituents with positive mesomeric contributions and possibly substituents with a high *p*-electron density.

At the same time compounds are known among perfluoroketone imines for which the *Z*/*E* transformations are achieved under the usual conditions and even at −60 °C. Judging from the ^{19}F NMR spectra, the acylimines[19], perfluoroacylimines[24,144], sulphinylimines[58], and sulphonylimines[23] of perfluoroketones belong to compounds of this class.

IV. THE REACTIVITY OF FLUORINE-CONTAINING IMINES

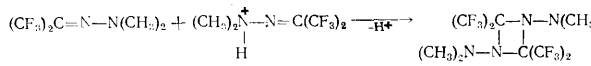
As unsaturated compounds with "amphoteric" properties, the non-fluorinated imines readily interact with electrophiles and nucleophiles. Under anhydrous conditions, they are readily protonated by acids with formation of iminium salts, interact with halogens and alkylating and nitrosating reagents, combine with alcohols, thiols, and amines, and react with organometallic compounds. Iminium salts interact particularly readily with nucleophiles.

As unsaturated compounds of the electron-donating type, imines enter into certain pericyclic reactions, particularly the [2 + 1]-, [2 + 2]-, and [2 + 3]-cycloaddition reactions. Azomethines, iminium salts, and acylimines are most reactive in these processes; compounds of the last type also possess dienophilic properties. The coordination-unsaturated character of the imine bond determines many isomeric and tautomeric transformations of imines of the hydrocarbon series.

The reactivity of the fluorine-containing imines differs significantly from that of their non-fluorinated analogues. The differences are considered below in relation to reactions with electrophiles and nucleophiles and also cycloaddition reactions.

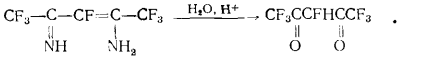
1. Reactions with Electrophiles

In most cases polyfluorinated imines are weak or even extremely weak bases. Under anhydrous conditions, they are therefore frequently indifferent to acids and do not manifest properties due to the formation of iminium salts. Only the hydrazones of fluorine-containing aldehydes and ketones are apparently protonated by strong acids, as shown by the electrophilic cooperative effect of sulphuric acid in the dimerisation of hexafluoroacetone dimethylhydrazone described by Wright and Zollinger[53]:

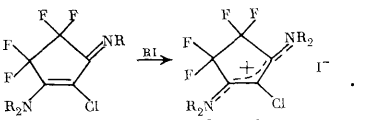


There are also data concerning the acid-catalysed reactions of partly fluorinated *N*-fluoroimines, which are attributed to the cleavage of the N—F bond by protic and Lewis acids[8]. Fully fluorinated *N*-fluoroimines do not interact even with sulphuric and fluorosulphonic acids[10]. Perfluoroketone perfluoroacylimines are indifferent to anhydrous acids on heating, which is used in their purification[50,61].

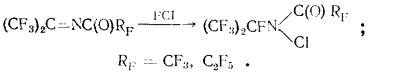
At the same time aqueous solutions of acids decompose fluorine-containing imines[85,86,89,96,99,101], which makes it possible to regard these compounds as convenient precursors of carbonyl and other compounds, for example[99]:



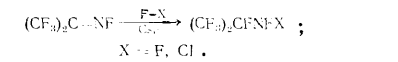
In view of their low basicity and weak nucleophilic properties, the alkylation of fluorine-containing imines has been hardly investigated. An example of such a reaction is provided only by the interaction of cyclic iminoenamines with alkyl iodides[93], where the alkylation is promoted by the additional stabilisation of the iminium ion by dialkylaminovinyl groups:



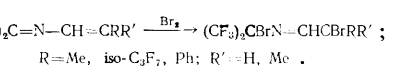
Among the halogens, only gaseous fluorine adds to the C=N bond of fluorine-containing imines. Thus perfluoroderivatives of saturated amines are isolated together with the perfluoro-derivatives of *N*-fluoroimines in the fluorination of nitriles and various imines in the gaseous and solid phases[8]. Chlorine fluoride, which readily adds to the C=N bond in *N*-fluorodihalogenocarbonylimines[8] and hexafluoroacetone perfluoroacylimines, have similar properties[144]:



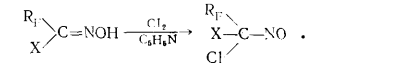
It is noteworthy that exhaustive fluorination of imines frequently takes place in the presence of alkali metal fluorides, the most active of which is CsF. Thus hexafluoroacetone imine has been converted into the *N*-fluoroimine on fluorination in the presence of KF and into the perfluoroisopropyldifluoroamine in the presence of CsF.[122] In the presence of CsF, hexafluoroacetone *N*-fluoroimine combines with chlorine fluoride[8]:



The chlorination and bromination of fluorine-containing imines do not usually take place in the absence of a catalyst. Only the interaction of bromine with hexafluoroacetone alkenylimines, leading to 1,4-addition products, has been described[119]:

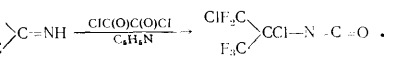


However, many reactions of the compounds considered with halogens and other electrophiles have been achieved in the presence of bases. The interaction of perfluoroketone oximes and polyfluoroalkylhydroamoyl halides with chlorine in pyridine leads to nitrosoperhalogenoalkanes[141,145] (the Piloti reaction):

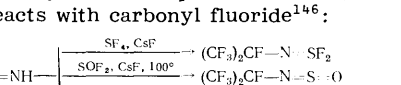


On chlorination in the presence of CsF and bromination in the presence of KF, perfluoroketine imines have been converted into the corresponding halogenoimines[122] (see above).

Chloropentafluoroacetone imine interacts smoothly with oxalyl chloride in pyridine, which leads to 1,2-dichloropentafluoroisopropyl isocyanate[146]:

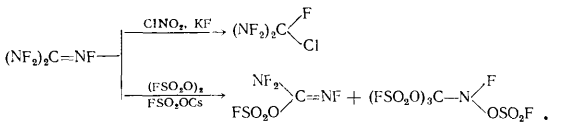


Hexafluoroacetone imine interacts with sulphur tetrafluoride[147] and thionyl fluoride[148] in the presence of caesium fluoride as the catalyst; in the presence of KF, hexafluoroacetone imine reacts with carbonyl fluoride[146]:

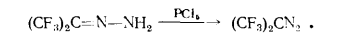


In the absence of catalysts, such reactions can be achieved only when the explosive hexafluoroacetone lithioimine is used (see above).

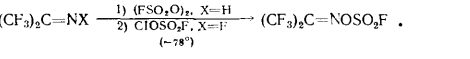
The interactions of pentafluoroguanidine with nitryl chloride catalysed by KF [149] and with peroxodisulphuryl difluoride in the presence of caesium fluorosulphate[150] have been described:



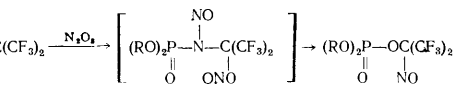
Non-catalysed reactions of electrophiles with fluorine-containing imines are also known. Thus hexafluoroacetone hydrazone is oxidised to bis(trifluoromethyl)-diazomethane on treatment with PCl_5:[60]



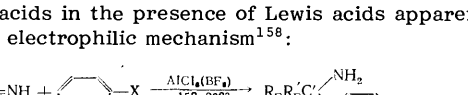
Substitutional fluorosulphonation of hexafluoroacetone imine by peroxodisulphuryl difluoride[151] and the reactions of halogenofluorosulphates with pentafluoroguanidine[152,153] and hexafluoroacetone fluoroimine[154] take place readily:



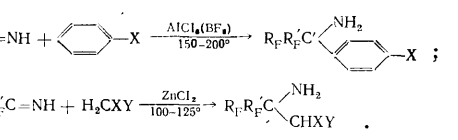
Hexafluoroacetone imine reacts with boron halides under mild conditions[155,156]:



The transformations of hexafluoroacetone dialkoxyphosphoryl-imines in the reactions with N_2O_3 are also of interest[157]:



The reactions of perfluoroketone imines with aromatic compounds or CH acids in the presence of Lewis acids apparently proceed via an electrophilic mechanism[158]:



It is evident from the data presented that fluorine-containing imines possess an unusual ability to interact with electrophiles. The protonation, alkylation, acylation, and electrophilic reactions, which take place readily with the non-fluorinated analogues and usually proceed via three-centre transition states, are not characteristic of these compounds. Fluorine-containing imines interact fairly vigorously only with reagents capable of electrophilic addition via a four-centre transition state (nitrosating agents, boron halides, and probably halogenofluorosulphates). Analogous behaviour is to some extent characteristic also of the reactions of electrophiles with polyfluoroalkenes[159].

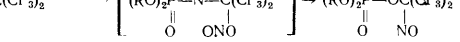
The available data also show that, as fluorine or polyfluoroalkyl groups accumulate at the imine bond, its ability to interact with electrophiles is sharply reduced. At the same time there is an increase of the probability of the reaction of fluorine-containing imines with electrophiles via a nucleophilic mechanism, which is also characteristic of polyfluoroalkenes[160]. The above finding suggests that one may expect an appreciable expansion of the range of reactions of fluorine-containing imines with electrophiles, many of which may acquire applied importance.

2. Reactions with Nucleophiles

In terms of the character of their reactivity with respect to nucleophiles, the fluorine-containing imines known at present can be divided into two groups. *N*-Polyfluoroalkyl-substituted mono- and di-fluorocarbonylimines, polyfluoroalkylhydroxamoyl fluorides, and certain *N*-fluoroimines should be included in the first group. All these compounds form predominantly or exclusively products of the substitution of the fluorine atom and the carbon atom of the imine group on interaction with nucleophiles of the type H–X. Numerous examples of reactions of this type have been published in a book[5] and in a review[6].

This character of the reactivity of the fluorine-containing imines of the first group is apparently associated with the increased asymmetry of the π orbital of the C=N bond due to the effects of the fluorine atom; this results in the elimination of the possibility of the concerted addition of the nucleophile and the process takes place in a stepwise manner.

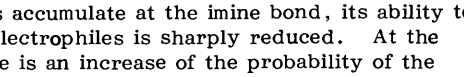
The absence of direct correlations between the nucleophilic properties of the reactants and the conditions of their reactions with *N*-trifluoromethyldifluorocarbonylimine (pentafluoro-2-azapropene) may be quoted in support of these ideas[6]. Proof of the impossibility of concerted reactions of compounds of this type has been obtained in a study of the interaction of polyfluoroalkylhydroxamoyl halides with triethylamine[161–165] where nitrile oxides should have been formed as a result of the concerted dehydrohalogenation. It was shown in the above studies that the mode of reaction depends little on the structure of the polyfluoroalkyl group and is determined exclusively by the nature of the halogen at the C=N bond. Thus, whereas the interaction of hydroxamoyl fluorides with triethylamine leads to oligomers under any conditions in the presence of dipolarophiles and in their absence[162], i.e.



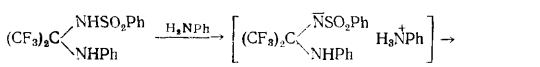
the corresponding hydroxamoyl chlorides and particularly hydroxamoyl bromides are converted by triethylamine under mild conditions into the corresponding nitrile oxides, detected by the presence of the [2 + 3]-cycloaddition products[163–165].

Acyl-, sulphinyl-, and sulphonyl-imines should be included in the second group of fluorine-containing imines, which react with nucleophiles to form addition products. Polyfluoroketone sulphonylimines have been most widely investigated in reactions with nucleophiles[166–173].

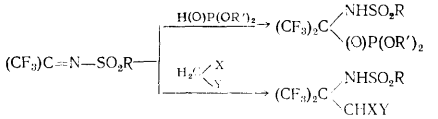
It has been shown[166–168] that polyfluoroketone methane- and benzenesulphonylimines interact vigorously with proton-containing nucleophiles and in many instances such reactions can be carried out unambiguously only in dilute solutions with cooling and slow introduction of the nucleophile into the reaction medium. Under optimum conditions, the reactions with aliphatic alcohols, α,β-unsaturated alcohols, ethylene chlorohydrin, and phenol (0–20 °C), thiols (−40 °C), amines (−50 to −40 °C), carboxylic acid amides (including their fluoro-derivatives), urea, and sulphonamides (50–60 °C) take place almost quantitatively:



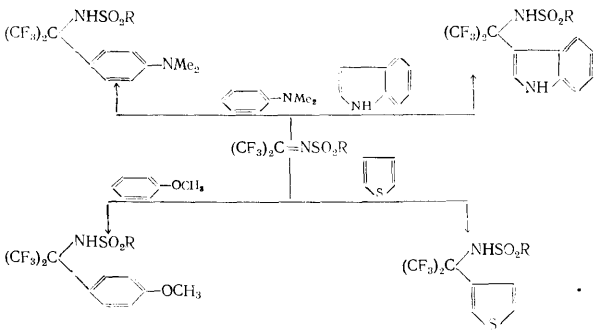
Polyfluoroketone sulphonylimines interact particularly vigorously with fairly strong bases. In this case there is a possibility of side reactions due to the appearance of an excess of the base in the reaction medium[166,167]:



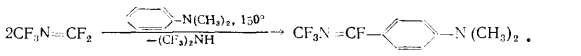
The reactions of polyfluoroketone sulphonylimines with PH and CH acids such as dialkyl phosphites (20 °C),[169] malonic and acetoacetic esters, and acetylacetone (20–50 °C) take place under mild conditions in the absence of catalysts[170]:



The π-electron-donating aromatic compounds, namely *N*,*N*-dimethylaniline (−40 °C),[171] indole (20 °C),[172] and anisole and thiophen (50–60 °C),[171,173] are unusually readily alkylated by polyfluoroketone sulphonylimines. The alkylation takes place regiospecifically at the site of maximum π-electron density in the ring:

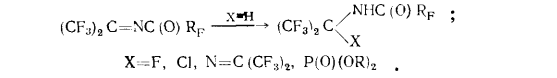


In all these reactions polyfluoroketone sulphonylimines behave as "mild" π-acids, which has been confirmed by the method of competing reactions[168]. This feature is responsible for the concerted mechanism of the addition reaction, which constitutes a significant difference between the sulphonylimines and the imines of the first group, for which many of the reactions described above either do not occur or require extremely severe conditions, for example[174]:

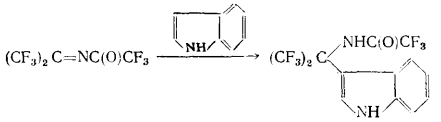


Hexafluoroacetone perfluoroacylimines, sulphinylimines, dialkoxyphosphorylimines, and acylimines, which are similar to sulphonylimines as regards the conditions of their reactions with nucleophiles, are distinguished by an extremely low energy barrier to *Z*/*E* transformations.

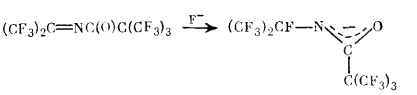
Hexafluoroacetone perfluoroacylimines are apparently even stronger π-acids than sulphonylimines. Together with the usual nucleophiles[24,108], they combine under mild conditions with hydrogen halides[144], hexafluoroacetone imine[73], and dialkyl phosphites[175] in the absence of catalysts:



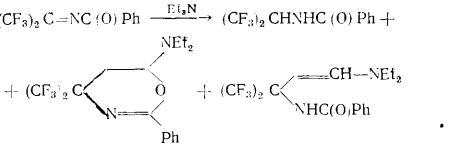
Hexafluoroacetone trifluoroacetylimine alkylates indole exothermically (on cooling)[172]:



A single example of the interaction of acylimines with the fluoride ion is known. It has been shown[106] that hexafluoroacetone perfluoropivaloylimine combines with caesium fluoride in an exothermic reaction, forming a salt stable up to 130 °C:



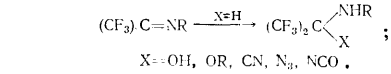
According to the available data, hexafluoroacetone sulphonylimines react exothermically with alcohols, thiols, and amines[58], while hexafluoroacetone dialkoxyphosphorylimines undergo exothermic reactions with water and alcohols[57]. At 20 °C alcohols, amines, and sulphonamides add to trifluoroacetaldehyde sulphonylimines[176]. Polyfluoroketone acylimines are highly reactive in reactions with alcohols thiols, amines, and acid amides[20,56]. The electrophilic properties of hexafluoroacetone acylimines are so pronounced that they are capable of "abstracting" a hydride anion from a triethylamine molecule[177]:



Other fluorine-containing imines are less reactive with respect to nucleophiles: polyfluoroketone imines unsubstituted at the nitrogen atom, aliphatic polyfluorinated azomethines, anils, hydrazones, azines, and *N*-fluoroimines. They constitute, as it were, an intermediate group of imines between difluoro- or fluoro-carbonylimines, on the one hand, and sulphonyl- or acyl-imines, on the other.

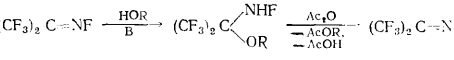
All these compounds combine vigorously with highly basic nucleophiles such as ammonia, amines, and hydrazines in the absence of catalysts, which has been demonstrated in relation to the reaction of hexafluoroacetone imines and anils[17,19,26,53,140], perfluoroguanidines, perfluoroamidines, and perfluoroketone *N*-fluoroimines[8,10], as well as hexafluoroacetone azine[115]. Thiols add to hexafluoroacetone anils[140] and alkenylimines[119] in the absence of catalysts and without heating. The conditions governing the interaction with hydroxy-compounds depend greatly on the nucleophilic properties of the latter and the electrophilic properties of the imine.

Thus hexafluoroacetone imine and its *N*-alkyl and *N*-aryl derivatives combine with lower alcohols on moderate heating or in the presence of catalysts without heating[17,26,78,140]. In the presence of basic catalysts, HCN, HN_3, HNCO, and acid alcohols interact with hexafluoroacetone imine[19,120]:



The addition is favoured by protophilic solvents capable of forming non-solvated anionoid species. Analogous features are characteristic also of the series of *N*-fluoroimines[8,10].

Even powerful electrophiles such as pentafluoroguanidine and pentafluoroamidines, which readily combine with lower alcohols, interact with weakly basic hydroxy-compounds only in the presence of nucleophilic catalysts[178,179]. Weaker electrophiles, for example polyfluoroketone *N*-fluoroimines, react even with aliphatic alcohols only in the presence of bases, forming adducts which are readily decomposed[8,10]:



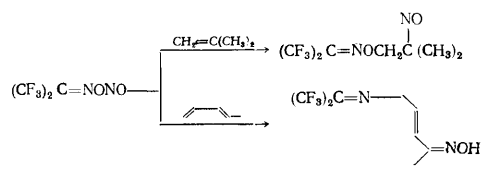
The extremely strong influence of steric factors on the conditions and even the possibility of the addition of the reactant to the C=N bond, characteristic also of the imines of the hydrocarbon series, must be regarded as a characteristic feature of the properties of the intermediate group of fluorine-containing imines, apart from the marked dependence of the conditions in their reactions with nucleophiles on the basicity of the latter. The increase of the bulk of the substituent at the imine nitrogen atom or at the nucleophilic centre of the reactant leads to a sharp alteration of the reaction parameters, so that in many instances even highly basic amines do not form adducts with fluorine-containing imines.

The next characteristic feature is that many of the fluorine-containing imines of this group are distinguished by an increased tendency towards the stepwise combination with nucleophiles. This determines the optimum conditions for their reactions with nucleophiles, the possibility of achieving the reactions with electrophiles with nucleophilic cooperation discussed above, and many unusual reactions of *N*-fluoroimines involving the formation of aza-anions[8]. In this respect the imines of the intermediate group, as it were, manifest the properties of difluoro- and fluoro-carbonyl-imines with the difference that they give rise to addition products instead of substitution products.

Thus a broad spectrum of the reactivities of the test compounds has been manifested in fluorine-containing imine–nucleophile systems: ranging from typical stepwise reactions to extremely mild concerted reactions. In the reactions of the first type one of the aspects of the reactivity of the dichlorocarbonylimines known in the hydrocarbon series is thrown into sharp contrast and is enhanced, while in the second type the unusual chemistry of iminium compounds is strongly manifested. At the same time the analogies noted above must be regarded as superficial. In reality the study of fluorine-containing imines as electrophiles led to the discovery of the most effective precursors of aza-anions, the strongest of the known "soft" π-acids, and a multiplicity of compounds with intermediate properties.

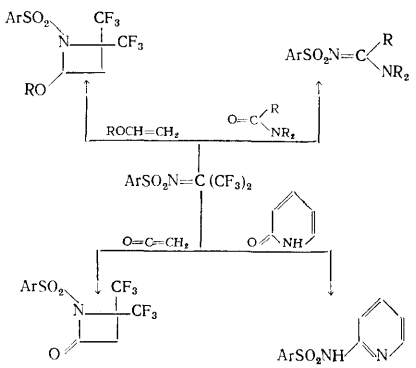
3. Cycloaddition Reactions

Various representatives of fluorine-containing imines have been investigated to unequal extents in cycloaddition reactions. Fluorine-containing oximes and their derivatives have not apparently been involved in cycloaddition hitherto. It has only been shown that in some of their reactions with unsaturated compounds, where one might have expected the formation of cyclic [2 + 2]- and [4 + 2]-adducts, acyclic substances were obtained. This happens on heating under severe conditions mixtures of hexafluoroisopropylidene-iminoxy-*N*,*N*-bis(trifluoromethyl)amine with polyfluoroalkenes[139] (see above). The nitrite of hexafluoroacetone oxime interacts analogously with polyfluoroalkenes at 180–190 °C [180] and with ethylenic compounds and 1,3-dienes at −50 to −15 °C:[181]



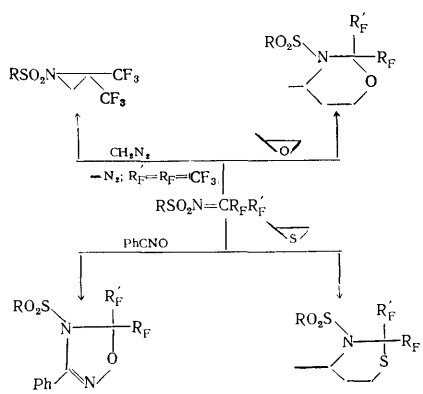
It may be that the many-centre π orbital of the derivative of the fluorine-containing oxime has no common symmetry elements with the π orbitals of alkenes and 1,3-dienes, i.e. the concerted [2 + 2]- and [4 + 2]-cycloaddition reactions are in this case prohibited.

Fluorine-containing azomethines are somewhat more reactive in cycloaddition processes than their hydrocarbon analogues and the tendency of these compounds towards cyclisation increases sharply with enhancement of the electron-accepting properties of the substituent at the imine nitrogen atom. Among the compounds of this series, polyfluoroketone sulphonylimines are the most reactive. It has been shown for hexafluoroacetone toluene-*p*-sulphonylimine that, under the conditions of intense cooling they react with keten and alkyl vinyl ethers to form cyclic [2 + 2]- adducts[21,22]. Hexafluoroacetone benzenesulphonylimine reacts vigorously with carboxamides via the cycloaddition–decomposition mechanism[182]:

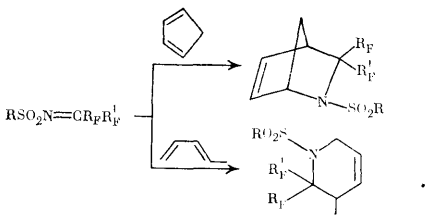


These data show that, as regards their tendency towards [2 + 2]-cycloaddition, fluorine-containing sulphonylimines have no equals in organic chemistry.

Polyfluoroketone sulphonylimines are extremely reactive also in [3 + 2]-cycloaddition. Their interaction with diazoalkanes takes place even at −60 °C and is accompanied by the elimination of nitrogen[168], which is characteristic of reactions of diazoalkanes controlled by the lowest unoccupied molecular orbitals (LUMO) of the imine and proceeds via a symmetrical transition state. Hexafluoroacetone benzenesulphonylimine readily interacts with benzonitrile oxide apparently via a stepwise pathway[161]. Polyfluoroketone sulphonylimines enter smoothly, under conditions typical for concerted reactions, into [3 + 2]-cycloaddition with oxirans and thi-irans[183,184]:

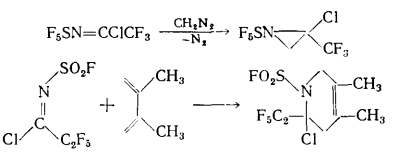


The [4 + 2]-cycloaddition of polyfluoroketone sulphonylimines takes place under unusually mild conditions[166]. They react smoothly with cyclopentadiene only with intense cooling (to −50 °C). *cis,trans*-Piperylene also enters into the reaction at a reduced temperature:

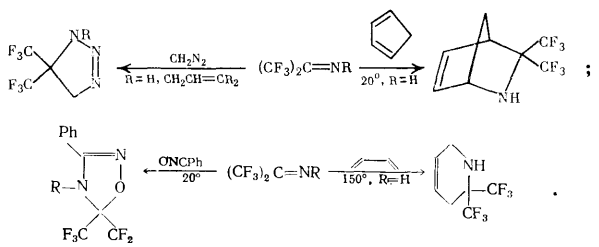


However, α,β-unsaturated aldehydes and ketones could not be involved in cycloaddition with polyfluoroketone sulphonylimines. The properties of polyfluoroketone sulphonylimines in [2 + 2]- and [4 + 2]-cycloaddition reactions described above are unusual and must be regarded as an exceptional case from the standpoint of the Woodward–Hoffman rules.

Other examples of the cycloaddition of highly electrophilic fluorine-containing imines are known. For example, trifluoroacetaldehyde toluene-*p*-sulphonylimine[37] readily forms a cyclic [4 + 2]-adduct with 2,3-dimethylbutadiene. Limiting cases of an unusually high tendency towards cycloaddition are known among fluorine-containing imines of other types, including halogenocarbonylimines[186,187]:



As the electron-withdrawing effects of the substituent and the imine nitrogen atom in fluorine-containing azomethines are reduced, their capacity for [2 + 2]-cycloaddition falls sharply. Thus hexafluoroacetone imine interacts with isobutene on heating above 200 °C to form a product of the "ene" reaction[188]. The reactivity in the [3 + 2]- and [4 + 2]-cycloaddition processes is reduced to a somewhat lesser extent[19,188–191]:



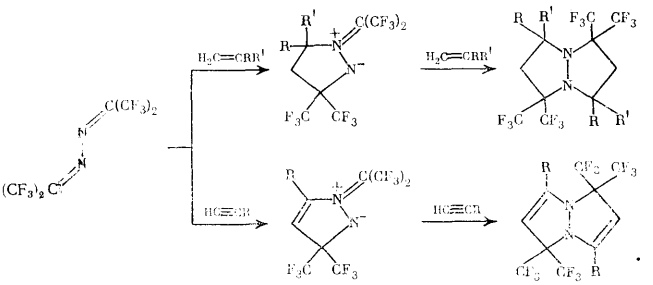
Attention should be drawn to the fact that diazomethane enters into these reactions as a 1,3-dipole[188,190] and not as a carbene precursor.

N-Fluoroimines are usually more reactive in cycloaddition reactions than fluorine-containing alkyl- and aryl-imines. They form fairly smoothly cyclic [3 + 2]- and [4 + 2]-adducts with diazomethane and 1,3-dienes respectively. Some of the compounds of this series, for example, perfluoroguanidines and amidines, are actually more reactive in [4 + 2]-cycloaddition reactions than polyfluoroketone sulphonylimines. However, in contrast to sulphonylimines, these compounds also give rise to [3 + 2]-cycloaddition products on reaction with diazomethane[8].

Fluorine containing hydrazones have been scarcely investigated in cycloaddition reactions. At the same time the spontaneous or acid-catalysed dimerisation of hexafluoroacetone *N*,*N*-dimethylhydrazone[53] (see above) under mild conditions constitutes important evidence indicating their capacity for cyclisation.

The pericyclic reactions of fluorine-containing azines and especially hexafluoroacetone azine occupy a special place in the chemistry of fluorine-containing imines. Attempts to involve this compound in [1 + 2]-cycloaddition lead either to the cleavage of the imine bond[109]:

or to products of the transformations of the primary cyclic [1 + 2]-adducts[55,116–119,192] (see above). Only keten[114] and diazomethane[115] could be involved in the reaction via the C=N bond with formation of cyclic [2 + 2]- and [3 + 2]-adducts respectively (see above). In other numerous reactions of hexafluoroacetone azine with unsaturated compounds, 1,5-diazabicyclo[3.3.0]octanes and 1,5-diazabicyclo[3.3.0]-octa-2,6-dienes are usually produced with the intermediate formation of cyclic azomethine-imines (see the communications by Tipping and co-workers[193,194] and Burger and co-workers[195,196] and the references quoted therein):



Thus the interaction of hexafluoroacetone azine with unsaturated compounds takes place as a two-stage cross [2 + 3]-cycloaddition. Ethylene, acetylene, monoalkyl- and monoaryl-substituted ethylenes and acetylenes, geminal dialkyl- and diaryl-ethylenes, alkyl vinyl ethers, alkoxyacetylenes, ynamines, certain cyclic alkenes, 1,3-dienes, acrylates, propiolates, etc. react with hexafluoroacetone azine via this pathway.

The intermediate azomethine-imines proved to be fairly stable in reactions of hexafluoroacetone azine with geminal dialkylethylenes, 1,3-dienes, alkoxyacetylenes, ynamines, etc. These compounds were isolated, their structure was demonstrated by spectroscopic methods and X-ray diffraction studies[193,196–200], and their properties were investigated. The intermediate products of these reactions served as precursors of 1,5-diazabicyclo[3.3.0]oct-2-enes, hexafluoroacetone alkenylhydrazones, and fluorine- and nitrogen-containing heterocycles (1,2-diazepines, pyrazoles, pyrazolines, pyrimidines, pyridine and triazine derivatives, etc.)[191–212].

The study of the pericyclic reactions of hexafluoroacetone azine enriched organic chemistry in new examples of intramolecular 1,3-, 1,4-, and cascade proton shifts, unusual 1,4-sigmatropic transitions of the CF_3 group, and examples of unusual intramolecular electrocyclic reactions. However, the observed characteristic features of the reactivity of azines as 1,3-dipolar systems of atoms realised in the C=N=N=C four-centre fragment must be regarded as the most important outcome of the study of hexafluoroacetone azine. The observed charactersitics of its reactions with unsaturated compounds reflect the features of [2 + 3]-cycloaddition reactions of the LUMO-controlled type and are important in synthetic organic chemistry.

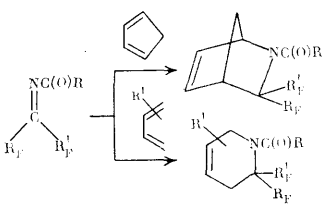
The studies of pericyclic reactions of fluorine-containing keten imines led to new advances in the chemistry of imines[11]. Their capacity for cycloaddition is greater than that of the known non-fluorinated triarylketen imines and, like the fluorine-containing azomethimes, increases appreciably as the

electron withdrawing effects of the substituents at the imine nitrogen atom become more pronounced. In contrast to triarylketen imines, fluorine-containing keten imines react exclusively at the imine bond in the [2 + 2]- and [3 + 2]-cycloaddition reactions with alkyl vinyl ethers, acetylenes, octafluoroisobutene, diazomethane, and nitrones. The dimerisation of fluorine-containing keten imines takes place analogously with nucleophilic cooperation by "soft" bases. Only dimerisation in the presence of "hard" bases and the epimerisation of these compounds involve the carbon–carbon bond. Thus the fluoroalkyl substituents in the cumulated C=C=N system exhibit more pronounced activating effects on the imine bond than on the carbon–carbon bond. The activating effects of perfluoroalkyl groups diminish the electron-donating properties of the imine group and hence the reactions controlled by the highest occupied molecular orbitals, characteristic of hydrocarbon keten imines, are replaced by the LUMO-controlled processes in the case of the fluorine-containing keten imines.

The appearance of unusual properties in the series of *N*-arylbis(trifluoromethyl)keten imines, where the imine group is linked to a conjugated system, proved to be an interesting consequence of the activating effect of the perfluoroalkyl groups. The primary pericyclic reactions are accompanied in this case by electrocyclic reactions involving aromatic systems. Formally both types of processes take place as [1 + 4]-cycloaddition in the presence of a carbenoid species and as [2 + 4]-cycloaddition in reactions with electron-donating alkenes or acetylenes. These mild reactions led to the prospect of the synthesis of hitherto inaccessible fluorine-containing derivatives of indole and quinoline and, in principle, they can be used also to synthesise other fluorine- and nitrogen-containing heterocycles[11].

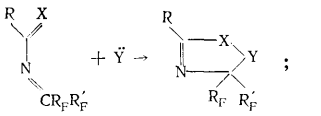
A large group of fluorine-containing imines, widely investigated in cycloaddition reactions, comprises the acyl-, thioacyl-, and iminoacyl-imines of polyfluoroketones. In contrast to azines, where the rigidity of the N–N bond prevents the formation of a four-centre π orbital in the molecule, free rotation of the acyl group at the nitrogen atom of the C=N bond is characteristic of compounds of this type, which creates conditions for the manifestation of the reactivity of both the isolated imine group and the conjugated C=N–C=X system.

The properties due to the isolated C=N bond have been investigated only in relation to the reactions involving the [4 + 2]-cycloaddition of cyclopentadiene and acyclic 1,3-dienes to polyfluoroketone acetyl- and perfluoroacyl-imines[213,214]:



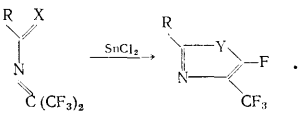
Perfluoroacylimines proved to be particularly reactive in these reactions. Cyclic adducts with cyclopentadiene can be isolated only when the reaction is carried out with intense cooling; perfluoroacylimines react at reduced temperatures even with acyclic 1,3-dienes. Hexafluoroacetone acetylimine enters into these reactions at room temperature.

The properties of polyfluoroketone acyl-, thioacyl-, and iminoacyl-imines as four-centre conjugated systems have been investigated much more widely. Carbenes, carbenoid species, and carbene precursors interact vigorously with these compounds via the [1 + 4]-cycloaddition mechanism:

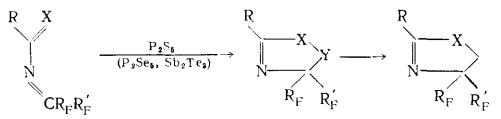


X=O, S, NH, NR, NAr; Y=CH_2, CCl_2, $C(OMe)_2$, C=NR, $P(OR)_3$.

Diazomethane[21], dichloro- and dimethoxy-carbenes and complexes of carbenes with chromium pentacarbonyl[83,109,212–217], isonitriles[83,216–220], and trialkyl phosphites[73,87,221–224] were made to undergo this reaction. Stannous chloride reacts similarly to carbonoid species, but the primary adduct decomposes and 1,3-azoles are formed[225,226]:

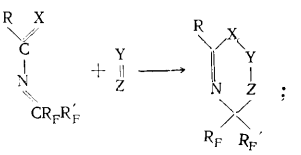


The affinity of acyl-, thioacyl-, and iminoacyl-imines for sulphur, selenium, and tellurium atoms proved to be unusually high. When the imines are heated with phosphorus pentasulphide or pentaselenide and antimony telluride, cyclic [1 + 4]-adducts are formed and then undergo a further exchange reaction[79,82,227–229]:



Y=S, Se, Te .

Reactions involving the [2 + 4]-cycloaddition of unsaturated compounds to acyl-, thioacyl-, and iminoacyl-imines of polyfluoroketones take place in most cases under extremely mild conditions. Electron-donating alkenes[21], alkyl vinyl ethers[21,230], keten[21,231], sulphenes and alkoxyacetylenes[232], aromatic aldehydes[233,234], α,β-unsaturated aldehydes[214,235], carboxylic acid nitriles[234], cyanamides[84], various alkenyl cyanides[214,236,237], and sulphoxides[238] undergo these reactions:



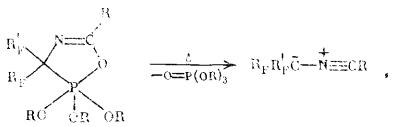
X=O, S, NH, NR, NAr .

The dienophilic properties of the compounds enumerated usually become more marked with enhancement of their electron-donating properties, which indicates the operation of LUMO-controlled mechanisms of these reactions.

Among the heterodienes of the series considered, the maximum activity is shown by perfluoroacylimines, which form cyclic [1 + 4]- and [2 + 4]-adducts as a rule under the conditions of intense cooling. These compounds must be regarded as the most reactive heterodienes among those known at present in organic chemistry.

The studies of the pericyclic reactions of polyfluoroketone acylimines enriched organic chemistry in many new examples of sigmatropic transformations and electrocyclic reactions, apart from the reactions discussed above. The cyclic

[1 + 4]-adducts of acylimines with phosphites, whose pyrolysis leads to highly reactive fluorine-containing nitrile-ylides, proved to be particularly interesting[239,240]:



A unique feature of these 1,3-dipoles is their unusually high capacity for [2 + 3]-cycloaddition not only to electron-donating unsaturated compounds but also to the C=N bond in nitrogen-containing heterocycles with formation of fluorine- and nitrogen-containing condensed systems.

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Numerous fluorine-containing analogues of imines of all known types have now been investigated on a fairly broad scale. These compounds proved in most cases to have more strained structures compared with their hydrocarbon analogues, which is the reason for their higher stability, the unique combination of their properties, and the specific features of the optimum conditions and pathways leading to their formation.

The introduction of fluorine and fluoroalkyl groups at the C=N bond usually suppresses the amphoteric character of the imines and imparts to them pronounced electrophilic properties, which depend in an unusually marked manner on the nature and positions of the fluorine-containing and other substituents at the imine bond. The effects resulting from the effect of the substituents at the highly polarisable C=N bond lead in this instance either to its marked inactivation or to a sharp increase of its ability to be involved in stepwise or concerted reactions. The chemistry of fluorine-containing imines therefore involves contrasting features. It is particularly rich in examples of extremely reactive and unreactive compounds with a C=N bond.

The above feature of the properties of fluorine-containing imines suggests that these compounds are ideal objects for theoretical studies. Comparative investigation of fluorine-containing imines and their non-fluorinated analogues at the electronic level constitutes at present one of the promising approaches to the creation of general molecular orbital models of organic compounds and their reactions.

Fluorine-containing azomethines, which reproduce many of the properties of non-fluorinated iminium salts, are of particular theoretical interest. The availability, stability, physicochemical properties convenient for investigations, and high reactivity suggest that the use of individual representatives of these compounds in the modelling of numerous biochemical reactions, involving the formation and metabolism of biogenic Schiff bases, is likely to be promising. Presumably more extensive studies of the steric effects and of the stereochemistry of reactions involving fluorine-containing imines will exert a fruitful influence on the understanding of the chemical nature of many processes involving vital activity.

The applied aspects of fluorine-containing imines have been associated for a long time only with the chemistry of the highly strained energy rich *N*-fluoroimines. However, during the last decade there has been a sharp increase of interest in various fluorine-containing imines as precursors of a wide variety of acyclic and alicyclic fluorine- and nitrogen-containing compounds. The data already accumulated at the present time suggest that fluoroimines can be usefully employed for the introduction of polyfluoroalkyl groups into a wide variety of specific structures, which leads to the possibility of their application in the syntheses of physiologically active substances and technically important products and also for the preparation of highly valuable materials. All these factors show that the advances achieved at the present time in the study of fluorine-containing imines constitute only the beginning of the development of an extremely rich field of the chemistry of organofluorine compounds with an electrophilic C=N bond.

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Nesmeyanov Institute of
Organoelemental Compounds,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 431-461 (1984) U.D.C. 547.413.5

The Chemistry of Perfluoroisobutene

Yu.V.Zeifman, E.G.Ter-Gabrielyan, N.P.Gambaryan, and I.L.Knunyants

The literature data on the methods of synthesis and reactions of the highly electrophilic perfluoroisobutene with nucleophiles as well as electrophiles are surveyed. The possibilities of employing this fluoro-olefin in organofluorine synthesis are discussed. The advances in the study of the perfluoro-t-butyl anion, generated from perfluoroisobutene and the fluoride anion, are considered in a special section.
The bibliography includes 199 references.

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I. INTRODUCTION

The ability of fluoro-olefins to react with nucleophiles, which distinguishes them radically from the hydrogen-containing analogues, is particularly pronounced in the case of perfluoroisobutene (PFIB), whose chemistry has developed vigorously since 1953. This fluoro-olefin is of special interest primarily because of its uniquely high electrophilic activity: PFIB reacts with almost all known nucleophiles and even the usual organic solvents, for example dimethylformamide or acetonitrile, are not sufficiently inert in relation to this compound. The properties of PFIB are close to those of activated olefins of the type of α,β-unsaturated carbonyl compounds or polycyano-olefins. At the same time the wide variety of the reactions of PFIB is determined by the lability of the fluorine atoms in the CF_3 group, characteristic of fluoro-olefins, and the possibility of further reactions of the addition products associated particularly with the high CH-acidity of the $(CF_3)_2CH$ group. All these factors, together with its ready availability, make it possible to employ PFIB widely in organofluorine synthesis.

The high electrophilicity of PFIB is due to the combination of the strong electron-accepting effects of the fluorine atoms and the CF_3 group on which is superimposed the capacity of the vinyl fluorine atoms for effective conjugation with the C=C bond. Indeed, the consecutive increase of the asymmetry of the molecule in the sequence $CF_2{=}CF_2 < CF_3CF{=}CF_2 < (CF_3)_2C{=}CF_2$ is accompanied by a gradual increase of the positive charge on the carbon atom of the CF_2 group, which has been confirmed by quantum-chemical calculations[1-3]. On the other hand, calculations for the molecules of PFIB and esters of perfluoromethylacrylic acid by the extended Hückel and CNDO methods[4] showed that their reactivity is determined by the dynamic properties of the distribution of electron density rather than the static distribution. The higher electrophilicity of perfluoromethylacrylate compared with PFIB can be explained by the greater ability of the alkoxycarbonyl group, compared with the CF_3 group, to stabilise the intermediate carbanions or carbanion-like transition states. From this point of view, the sharp increase of electrophilicity in the above sequence is caused in the first place by the growing stability of the carbanions: $NuCF_2\bar{C}F_2 < NuCF_2\bar{C}FCF_3 < NuCF_2\bar{C}(CF_3)_2$ (Nu is the nucleophile residue). Such variation of the state of the carbanion is evidently associated not only with the stabilising effect of the CF_3 group but also with the destabilisation of the carbanionic centre by the compact unshared electron pairs of the α-fluorine atoms.

The framework of the present review precludes a comparison of the electrophilic properties of PFIB and the lower fluoro-olefins in relation to specific examples. We shall only note that in all cases without exception PFIB is much more reactive in reactions with nucleophiles than, for example, hexafluoropropene. At the same time, the reactions of PFIB with electrophiles, if they occur at all, proceed with much difficulty. Nucleophilic catalysis therefore assumes special importance in such reactions, which reflects the change in the reaction mechanism from electrophilic in the case of non-fluorinated olefins and lower fluoro-olefins to nucleophilic for PFIB. Separate aspects of the chemistry of PFIB have already been discussed in a number of recent reviews[1-8]. However, the chemistry of this fluoro-olefin has not so far been fully considered.

II. PHYSICAL PROPERTIES AND METHODS OF SYNTHESIS

PFIB is a colourless highly toxic† gas[9] with a boiling point of 6.5 °C, which can be readily identified from the infrared[10] and ^{19}F NMR [7] spectra. Its reduction potential at the platinum electrode is −2.65 V.[11]

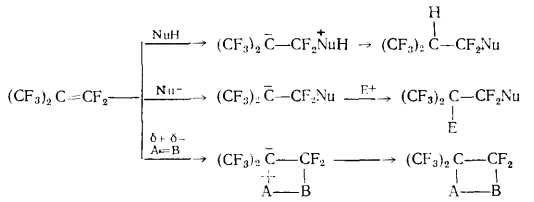
The main methods of synthesis of PFIB include thermolytic processes, which indicates a high thermal stability of this compound. PFIB is obtained by the pyrolysis of Teflon[12], tetrafluoroethylene[13], hexafluoropropene[14], and perfluorocyclobutane[10,15] at 700–750 °C (see also other communications [16-18]). It has been suggested that the synthesis of PFIB by pyrolysis involves the intermediate formation of difluorocarbene[13,19]. In addition, PFIB can be obtained by the dechlorination of 1,2-dichloro-octafluoroisobutane by zinc in dioxane or acetone[20], but this reaction is of limited practical interest, since the dichloride itself is obtained only on chlorination of PFIB.

III. REACTIONS WITH NUCLEOPHILES

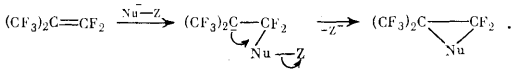
The chemistry of PFIB includes all the reactions with nucleophiles characteristic of fluoro-olefins. Addition to double bond of PFIB takes place when it interacts with

† PFIB is approximately 10 times more toxic than phosgene.

proton-donating nucleophiles. The conjugated nucleophilic addition reactions (the commonest instance is that of the reactions with participation of the F^- anion) as well as ionic cycloaddition of 1,2- or 1,3-dipolar compounds belong to the same type:

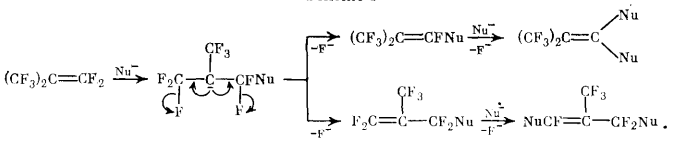


In those cases where the nucleophile is attached to a group Z capable of being split off in the form of an anion (or neutral molecule), the addition can be accompanied by intramolecular cyclisation [see Eqns.(3), (4), (6), and (7) below]:



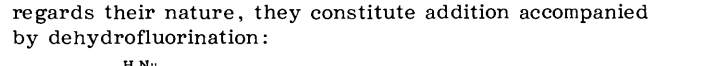
When PFIB interacts with conjugated nucleophiles, the vinyl fluorine atom is usually substituted. The same process is frequently accompanied by the addition of nucleophiles to PFIB, which distinguishes it sharply from the lower fluoroolefins for which addition is more typical. In many cases the products of the "allyl" substitution resulting from the elimination of an F^- anion from the CF_3 group are formed. Both "vinyl" and "allyl" products are usually capable of further reactions with nucleophiles, which leads to geminal substitution of 1,3-disubstitution (Scheme 1):

Scheme 1



The relative contributions of the vinyl and allyl substitutions are determined by the nature of the entering nucleophile and also by the reaction conditions. The vinyl substitution is facilitated in the interaction with nucleophiles which ultimately give rise to a substituent with an unshared electron pair as a result of the reaction. In other cases allyl substitution competes with this process to some extent [see Eqn.(9) below].

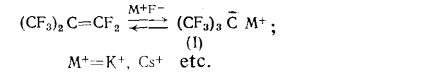
In certain reactions of PFIB both vinyl and fluorine atoms are substituted by an alkylidene residue, the imino-group, or a sulphur atom. However, these processes, which lead to the formation of cumulenes or heterocumulenes, can be classified only formally as substitution reactions, since, as regards their nature, they constitute addition accompanied by dehydrofluorination:



1. Reactions with Halide Ions

The Fluoride Ion

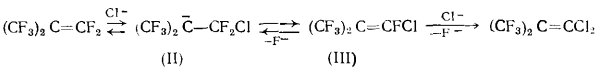
PFIB readily interacts with alkali metal fluorides (KF, CsF) in aprotic dipolar solvents with formation of the perfluoro-t-butyl anion (I). The reaction is reversible, so that the free fluoro-olefin is present in solution together with the anion (I).[7] The anion (I) is generated also in the reaction of PFIB with tetramethylformamidinium hydrogen fluoride[21] or hexamethylguanidinium fluoride[22] and in this case the equilibrium is displaced to a greater extent towards the anion (I), as shown by the ^{19}F NMR spectra:



In terms of their wide variety and importance for the chemistry of fluorocarbanions, the reactions of the anion (I) are of independent interest and will be considered in the concluding Section of this review. We shall only note that the anion (I) readily combines with a proton. Thus the interaction of PFIB with hydrogen fluoride in the presence of catalytic amounts of ammonium fluoride[23] or triethylamine[24] results in the formation of monohydroperfluoroisobutane $(CF_3)_3CH$. This reaction is important in the chemistry of PFIB because it accompanied the transformations of the latter in which the initial adducts are dehydrofluorinated.

The Chloride Ion

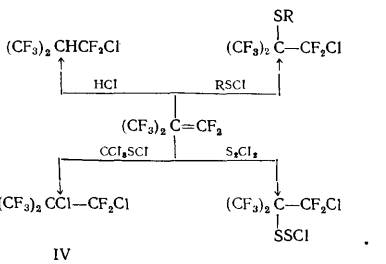
PFIB is also capable of combining with the Cl^- anion via the double bond with formation of the anion (II). This might have led to the exchange of chlorine for fluorine but under the usual conditions this reaction does not occur, since the equilibrium in the exchange is largely displaced towards the initial reactants. The exchange reaction was achieved in the presence of compounds which irreversibly bind the F^- anion. Thus fluorine is exchanged for chlorine in PFIB when the latter is treated with benzoyl chloride in the presence of pyridine; together with the monochloride (III), a certain amount of the *gem*-dichloride is formed under these conditions[25]:



(1)

The interaction of PFIB with phosphoryl chloride catalysed by triethylbenzylammonium chloride (TEBA) yielded the monochloride (III) and the dichloride $ClCF_2C(CF_3)=CFCl$.[25] Furthermore, TEBA or tertiary amines catalyse the hydrochlorination of PFIB [23] and the addition to the latter of aliphatic and aromatic sulphene chlorides[26] or sulphur monochloride[27]. It is of interest that the interaction of PFIB with sulphene chlorides containing electron-accepting groups, in the presence of the chloride ion, is of the halogenophilic type and leads to the chlorination of PFIB.[26] The dichloride (IV) has also been obtained on treatment of PFIB with chlorine under the conditions of nucleophilic catalysis[28] (Scheme 2):

Scheme 2



IV

In the absence of a catalyst, these reactions either do not occur at all or require very severe conditions [see Eqn.(13) below].

The Bromide Ion

Fluorine exchanges for bromine in PFIB on treatment of the latter with benzoyl bromide in the presence of pyridine. Together with the monobromide $(CF_3)_2C{=}CFBr$, disubstitution products are formed[25]. Under the conditions of nucleophilic catalysis, it has also been possible to achieve the hydrobromination of PFIB [23] and the addition of bromine to the latter[28] [see Eqn.(13)].

PFIB does not react with the iodide anion; hydriodic acid also does not add to PFIB under the conditions of nucleophilic reaction[23]. Iodoperfluoroisobutene has been obtained from the monochloride (III) by the exchange reaction with KI.[29]#

2. Reactions with *O*-Nucleophiles

Water and Hydrogen Peroxide

When PFIB reacts with water in acetone[30] or tetrahydrofuran (THF),[31] α-hydrohexafluoroisobutyric acid (V) is formed in a high yield. This is one of the most important reactions of PFIB in practice, particularly because the acid (V) is the starting compound for the synthesis of bis(trifluoromethyl)keten [32] and derivatives of perfluoromethacrylic acid[33]. Depending on the reactant ratio and the reaction conditions, the hydration of PFIB in the presence of triethylamine can yield the fluoride of the acid (VI), the acid (V), or its decarboxylation product—dihydroperfluoropropane[34]:

$$(CF_3)_2C{=}CF_2 \xrightarrow[-HF]{H_2O} \underset{(VI)}{(CF_3)_2CH{-}COF} \xrightarrow[-HF]{H_2O} \underset{(V)}{(CF_3)_2CH{-}COOH} \xrightarrow{-CO_2} (CF_3)_2CH_2 .$$

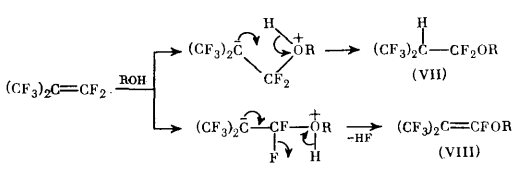
The alkaline epoxidation of PFIB leads to an epoxide[35-37] [see also Eqn.(4)], which has been suggested as a monomer[38,39]:

$$(CF_3)_2C{=}CF_2 \xrightarrow[NaOH]{H_2O_2} (CF_3)_2C(O{-}OH){-}CF_2 \xrightarrow{-OH^-} (CF_3)_2C(O){-}CF_2 . \qquad (3)$$

Alcohols

PFIB readily reacts with aliphatic alcohols[40-42] and cellulose[43]. The reaction results in the formation, apart from compound (VII), also of the vinyl ethers (VIII) (Scheme 3). It has been established that the saturated ethers (VII) are converted into the unsaturated ethers (VIII) under much more severe conditions than those in the reaction of PFIB with alcohols. On this basis, it is assumed that the ethers (VII) and (VIII) are formed independent of one another:

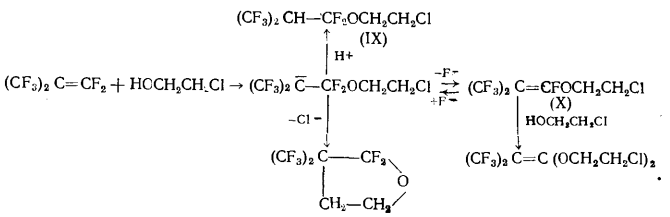
Scheme 3



Perfluoroisobutenyl derivatives of lithium and magnesium, which can be used to synthesise compounds containing the $(CF_3)_2CF{=}CF$ group, were obtained from chloro- and iodoperfluoroisobutenes[29].

The intermediate dipolar ion is stabilised mainly as a result of the protonation of the anionic centre but enhancement of the electron-donating properties of the residue R promotes the elimination of the F^- anion from the CF_2 group[40]. With increase of the acidity of the alcohols, their interaction with PFIB becomes more difficult. Thus CF_3CH_2OH, $HSCH_2CH_2OH$, and $ClCH_2CH_2OH$ react with PFIB under mild conditions only in the presence of basic catalysts[40], which tends to increase the fraction of the vinyl substitution products. For example, depending on the conditions, either the ethers (IX) and (X) or the acetal or bis(trifluoromethyl)keten can be obtained from PFIB and ethylene chlorohydrin[44,45]. The product of the intermolecular cyclisation of the intermediate carbanion is formed only under the conditions of thermodynamic control on interaction of the vinyl ether (X) with the F^- anion[45] (Scheme 4):

Scheme 4

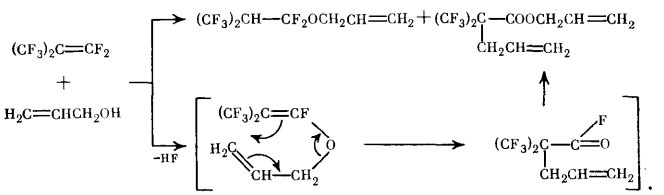


The addition of the enol of pentafluoroacetone to PFIB is catalysed by *N*-methylpyrrolidine or pyridine[46]:

$$(CF_3)_2C{=}CF_2 + CF_2{=}C(OH){-}CF_3 \rightarrow (CF_3)_2CHCF_2OC(CF_3){=}CF_2 .$$

The reactions of PFIB with allyl alcohols are of special interest. Together with the addition products, the products of the Claisen rearrangement of allyl vinyl ethers and not the ethers themselves are formed (Scheme 5):[47,48]

Scheme 5

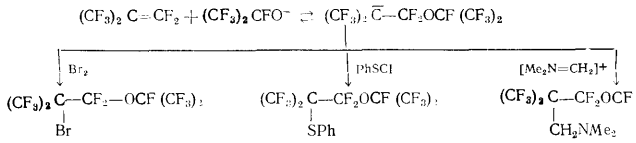


Propargyl alcohol and its homologues react analogously with PFIB and the migration of the propargyl group is accompanied by the acetylene–allene rearrangement[48]. It has been suggested that the products of all these reactions are formed as a result of the [3,3]-sigmatropic rearrangement of the intermediate fluorocarbanion[48].

The reactions of PFIB with sodium alkoxides in aprotic media lead to alkyl perfluoroisobutenyl ethers of bis(trifluoromethyl)keten acetals depending on the reactant ratio[49]. PFIB is apparently capable, in principle, of interacting also with alkali metal perfluoroalkoxides, but the reaction is reversible and the equilibrium is fully displaced towards the initial reactants (the perfluoroisopropoxide anion is a more effective leaving group than the fluoride anion). Indeed, in the presence of appropriate electrophiles it is possible to detect the formation of an intermediate carbanion and to obtain the products of the coupled perfluoroalkoxybromination or perfluoralkoxysulphenylation of PFIB. The alteration of the nature of the counterion leads to an analogous result: the interaction of PFIB with the salt $[Me_2N{=}CH_2]^+\bar{O}CF(CF_3)_2$

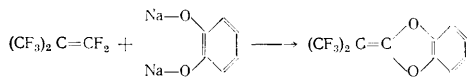
yields a fluorine-containing alkoxyamine as a result of the covalent binding of the intermediate carbanion to the methyleneimmonium cation (Scheme 6):[50]

Scheme 6



Phenols

On heating, PFIB reacts with phenol and resorcinol; only the addition products have been obtained as a result[51]. Like alkoxides, the phenoxides react in their turn with PFIB under mild conditions and give rise to the products of the vinyl monosubstitution[52,53] and disubstitution[54,55]. When PFIB reacts with the disodium salt of catechol, a cyclic keten acetal is formed[56]:

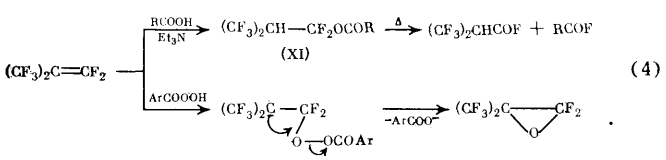


Acids and Peracids

In contrast to derivatives of perfluoromethacrylic acid[33], PFIB does not react with carboxylic acids in the absence of a catalyst. Acetic and benzoic acids add to PFIB only in the presence of triethylamine. The resulting adducts (XI) decompose into two acid fluorides on treatment with triethylamine[57] or on thermolysis[58].

Despite the fact that the introduction of electronegative substituents into the olefin molecule usually hinders the Prilezhaev epoxidation, PFIB readily interacts with aromatic peracids to form an epoxide (Scheme 7). The reaction mechanism is apparently inverted in this case and the peracid functions as a nucleophile[59]:

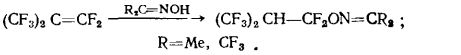
Scheme 7



(4)

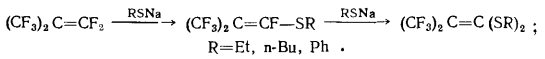
Derivatives of Hydroxylamine

PFIB readily comines with acetone[60] and hexafluoroacetone[61] oximes:



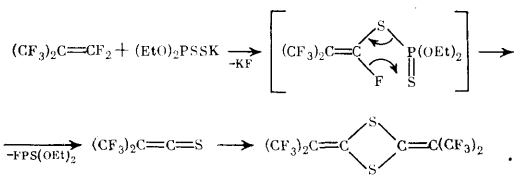
3. Reactions with *S*-Nucleophiles

The interactions of PFIB with benzylmercaptan[62], allylmercaptan[63], and thiophenol[26] lead mainly to addition products. Depending on the conditions, mono- or di-substitution products have been obtained in the reactions with mercaptides[64] and thiophenoxide[65]:

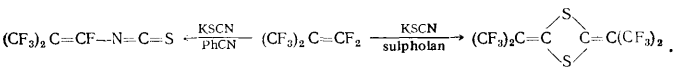


Disubstitution with formation of the bis(trifluoromethyl)-thioketen dimer takes place with PFIB reacts with potassium diethyl phosphorodithioate (Scheme 8):[66] the monosubstitution product could not be isolated owing to its spontaneous decomposition:

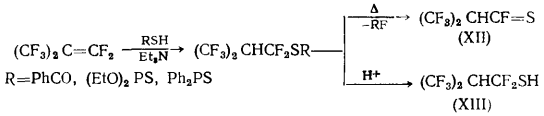
Scheme 8



This reaction is of preparative importance. The interaction of PFIB with the salts of other thiolo-acids leads to the same result[67-69]. It is of interest to note that, in the reaction of PFIB with KSCN, the thiocyanate ion exhibits the properties of an ambident nucleophile[70]:



Thiolo-acids add to PFIB in the presence of triethylamine as the catalyst. Like their oxygen analogues [see Eqn.(4)], the resulting adducts decompose on thermolysis with formation of the thioacid fluoride (XII). Acid hydrolysis of the adducts leads to the mercaptan (XIII) with two fluorine atoms in the α-position[58].

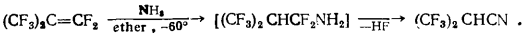


4. Reactions with *N*-Nucleophiles

PFIB readily reacts with ammonia and amines and the tendency towards the formation of unsaturated products is then enhanced.

Ammonia

PFIB vigorously combines with ammonia. Subsequent dehydrofluorination leads to hexafluoroisobutyronitrile, the low yield of which can be explained by its extreme instability in relation to ammonia[41]:



The much lower reactivity of hexafluoropropene in this reaction permits the employment of the latter for the elimination of PFIB from hexafluoropropene[71].

Primary Amines

The interaction of PFIB with primary amines leads to α-hydrohexafluoroisobutyroimidoyl fluorides, the amidines derived from this acid, or bis(trifluoromethyl)keten imines (Scheme 9):[72,73]

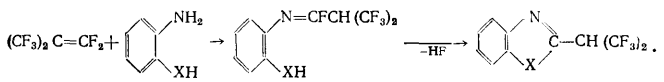
Scheme 9

$$(CF_3)_2C{=}CF_2 \xrightarrow[-HF]{RNH_2} (CF_3)_2CHCF{=}NR \begin{cases} \xrightarrow{-HF} (CF_3)_2C{=}C{=}NR \\ \xrightarrow{RNH_2} (CF_3)_2CHC(NR)(NHR) \end{cases} \quad (5)$$

In the reaction of PFIB with an excess of *p*-toluidine, the corresponding amidines undergo further reactions: derivatives of azetidine and quinoline were obtained under these conditions[74].

Keten imines can be obtained either by the direct interaction of PFIB with primary amines catalysed by triethylamine (in this case the PFIB–Et_3N system behaves simultaneously as the acceptor of the HF evolved) or with preliminary isolation of imidoyl fluorides and subsequent dehydrofluorination with powdered KOH in ether or with the adduct $BF_3.Et_3N$§. The interaction of PFIB with primary amines in the presence of CaF does not stop at the stage involving the formation of ketene imines but leads to their cyclic adducts with PFIB [see Eqn.(12) below].

When PFIB was allowed to react with *ortho*-substituted anilines, the products of the cyclisation of the intermediate imidoyl fluorides were obtained[56] (see also Nakai et al.[75]):

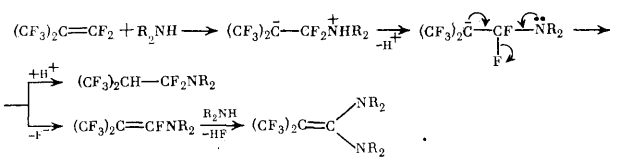


X=O, S, NH

Secondary Amines

The interaction of PFIB with secondary amines leads to both addition products and unsaturated products (Scheme 10) and the available data do not permit a rigorous distinction to be made (as in the reaction with alcohols) between situations where the unsaturated products are formed as a result of direct vinyl substitution or as a result of the dehydrofluorination of the adducts formed initially[76–78]:

Scheme 10

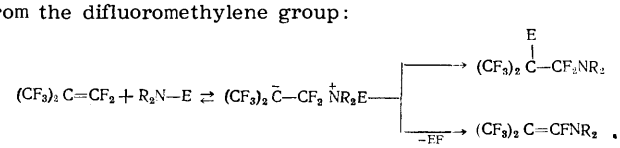


It has been suggested[76] that the presence of electron-donating substituents at the nitrogen atom increases the ability of its electron pair to "expel" the fluoride ion from the intermediate carbanion. The reactions of PFIB with highly basic secondary amines therefore lead to unsaturated products, while the reactions with weakly basic amines lead to the formation of addition products. The interaction of PFIB with dimethylamine or piperidine in the presence of an excess of the base leads to bis(trifluoromethyl)keten aminals. The corresponding aminal could not be obtained by the reaction with diethylamine, apparently owing to the influence of steric factors in this reaction[79].

§ This reagent is particularly convenient in the synthesis of keten imines which readily dimerise in the presence of traces of bases.

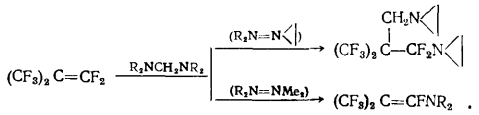
Tertiary Amines

The interaction of PFIB with tertiary amines leads to the formation of a dipole ion. When a group capable of cationoid abstraction is present at the nitrogen atom, the ion is stabilised either via the migration of this group to the carbanionic centre or via its elimination with a fluorine atom from the difluoromethylene group:



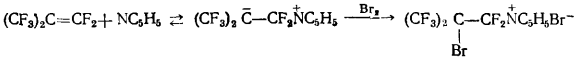
Thus, depending on the character of the substituents at the nitrogen atom, the insertion products or the products of the substitution of a fluorine atom by a dialkylamino-group have been obtained by the reaction of PFIB with tetra-alkyldiaminomethanes (Scheme 11):[80]

Scheme 11



The latter case evidently obtains also in the interaction of PFIB with *N*-trimethylsilylpiperidine[79].

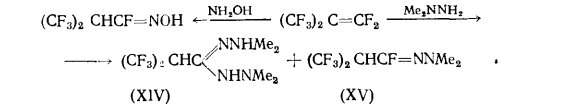
The formation of a dipolar ion from PFIB and R_3N has been confirmed in the study of the reaction of PFIB with pyridine in the presence of bromine; this yielded a coupled addition product[28]:



There exist many indirect data indicating the reversible addition of R_3N to PFIB. Thus the dimerisation of bis(trifluoromethyl)keten imines by tertiary amines is retarded in the presence of PFIB by a factor greater than 100.[72]

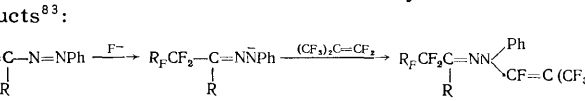
Hydroxylamine, Organic Derivatives of Hydrazine, and Hydrazoic Acid

When PFIB reacts with free hydroxylamine, the fluoride of α-hydrohexafluoroisobutyrohydroxamic acid is formed[81]. The reaction of PFIB with 1,1,-dimethylhydrazine gives rise to the hydrazine derivatives (XIV) or (XV), depending on the reactant ratio[82]:



(XIV) (XV)

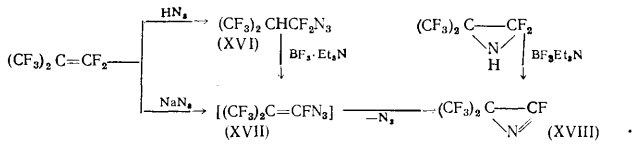
The interaction of PFIB with phenylazo-olefins in the presence of CsF results in the formation of vinyl substitution products[83]:



PFIB combines with 3,3-dimethylaziridine[84]. An addition product has been obtained from PFIB and hydrazoic acid, generated *in situ* from NaN_3 and sulphuric acid in dimethylformamide[85]. PFIB reacts even more readily with sodium azide[85,86]. The azirine (XVIII), formed as a result of the spontaneous decomposition of the unsaturated azide (XVII),

then polymerises under the influence of the nucleophiles present in the reaction mixture. However, it was obtained under neutral conditions by the dehydrofluorination of the saturated azide (XVI) or 3,3-difluoro-2,2-bis(trifluoromethyl)aziridine by the complex $BF_3.Et_3N$ (Scheme 12):

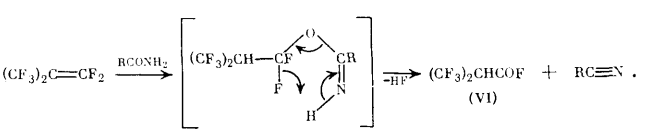
Scheme 12



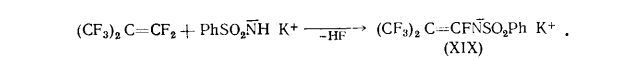
Amides and Sulphonamides

The electrophilic properties of PFIB are sufficiently strong for it to react with carboxylic acid amides in the absence of bases[87]. When PFIB was allowed to react with acetamide or benzamide in diglyme, the acid fluoride (VI) and the corresponding nitriles were obtained (Scheme 13). Evidently in this case the amides undergo *O*-alkylation with formation of unstable iminoesters, which decompose subsequently like the acyl derivatives of α,α-difluoroalcohols [see Eqn.(4)]:

Scheme 13



The much less basic benzenesulphonamide and urethane react with PFIB only in the presence of bases. PFIB readily reacts with the potassium salt of benzenesulphonamide to form the adduct (XIX) of *N*-phenylsulphonylketen imine with KF:[87]

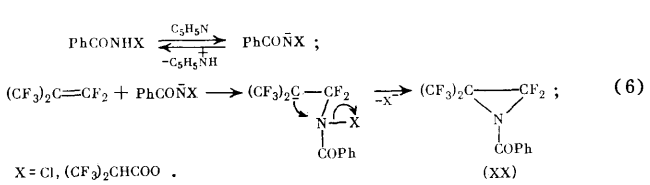


The reaction of PFIB with urethane takes place in the presence of KF as the catalyst and leads to the adduct of the corresponding keten imine with PFIB [see Eqn.(12) below]

N-Nucleophiles Containing Leaving Groups

When PFIB interacts with *N*-chloro- or *N*-acyloxy-benzamide in the presence of bases, *N*-benzoylaziridine (XX) is formed in a satisfactory yield (Scheme 14). This reaction, which constitutes nucleophilic cyclisation of PFIB, is an example of the fixation of the amide anion formed as an intermediate in the Hofmann and Lossen rearrangements by the interaction with the electrophilic C=C bond[88]:

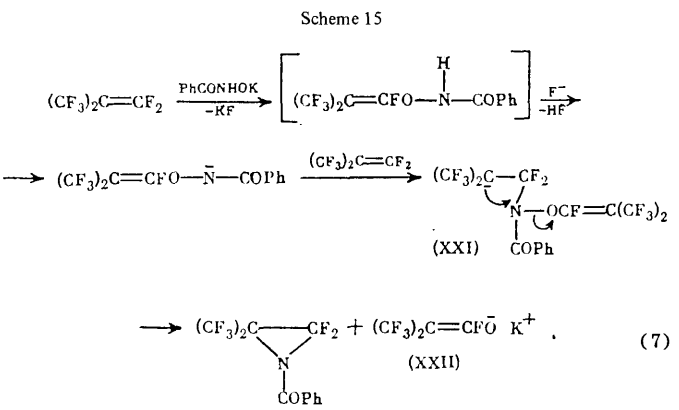
Scheme 14



(6)

The reaction of PFIB with the potassium salt of benzohydroxamic acid proceeds via an analogous route (Scheme 15). In this case the carbanion (XXI) cyclises and the mesomeric anion (XXII) plays the role of the leaving group[88]:

Scheme 15

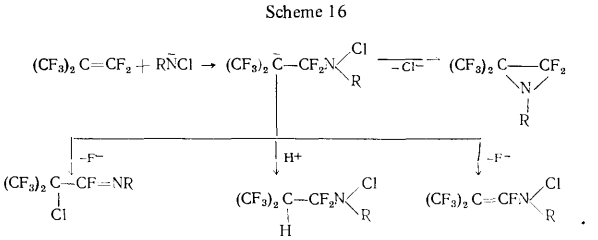


(7)

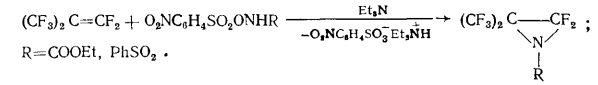
The formation of the aziridine (XX) was also detected in the reaction of PFIB with $Me_3\overset{+}{N}-\overset{-}{N}COPh$.[88]

When various *N*-chloroamides were involved in the nucleophilic cyclisation reaction, it was observed that products other than aziridines are also formed; this is associated with the low effectiveness of the Cl^- anion as the leaving group and also with the tendency of the chlorine in the *N*-chlorocompounds to undergo cationoid abstraction (Scheme 16):[89]

Scheme 16



The cyclisation of PFIB with the aid of *N*-(*p*-nitrobenzenesulphonyloxy)amides takes place much more unambiguously[89]:

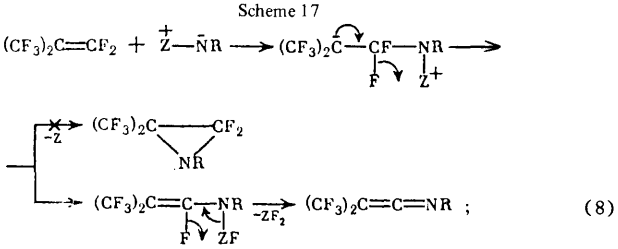


These reagents have been used successfully for the cyclisation of other highly electrophilic unsaturated fluorine compounds[89].

It has been established that PFIB does not form cyclic adducts with acylnitrenes generated by the photolysis of benzoyl[88] or alkoxycarbonyl azides[89]; this confirms the nucleophilic mechanism of the formation of the fluorine-containing aziridines.

In the interaction of PFIB with iminophosphoranes[90] or iminosulphuranes[91], rings are not formed either. The only pathway in these reactions involves vinyl substitution in accordance with Scheme 17 accompanied by the β-decomposition of the intermediate fluorides [see Eqn.(11)]:

Scheme 17



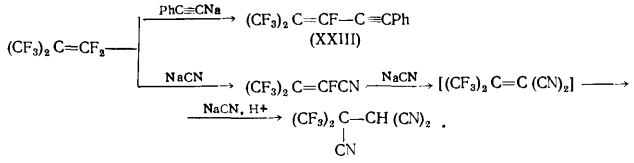
(8)

Z = Ph_3P, R = Ph; Z = Me_2S, R = COOEt.

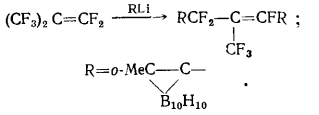
5. Reactions with *C*-Nucleophiles

Organometallic Compounds

The replacement of the vinyl fluorine atom by the CN group is readily achieved by the reaction of PFIB with NaCN and the resulting nitrile is capable of further reaction with the cyanide[92]. The reaction of PFIB with sodium phenylacetylide in ether results in the formation of the enyne (XXIII):[93]

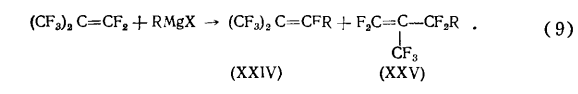


When PFIB was allowed to react with aryl-lithium compounds, a series of vinyl mono- and di-substitution products were obtained; the latter exhibit a high contraceptive activity[94,95]. PFIB reacts with 2-lithio-1-methyl-*o*-carbaborane to form a 1,3-disubstitution product[96]:



The corresponding derivative of *m*-carbaborane gives rise to the product of the usual vinyl substitution[97].

PFIB reacts readily with alkyl- and benzyl-magnesium halides with formation of vinyl and allyl substitution products[98–100]:



(9)

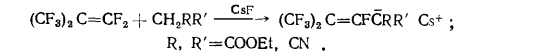
The terminal olefins (XXV) are readily converted into the inner olefins (XXIV) by Lewis bases¶ or acids. This apparently explains the finding that, when PFIB interacts with arylmagnesium halides, it is possible to identify only the inner olefins (XXIV). The corresponding terminal olefins should contain the highly mobile "benzyl" fluorine atom, a result of which they are converted into the olefins (XXIV) under the reaction conditions.

Compounds with Active Methylene and Methyl Groups

PFIB does not react with malonic ester in the absence of bases but, with catalysis by triethylamine, it gives rise to a mixture of products containing the alkylidenemalonic ester (XXVI), the allene (XVII), and the pyran (XXVIII).[101] The reaction of PFIB with sodiomalonic ester leads to the same result†. The allene and pyram are formed as a result of the dehydrofluorination of the alkylidenemalonic ester (XXVI) via two pathways: with elimination of the vinyl fluorine atom or the fluorine atom from the CF_3 group; in the latter case the 1,3-diene cyclises to a pyran (Scheme 18):[100]

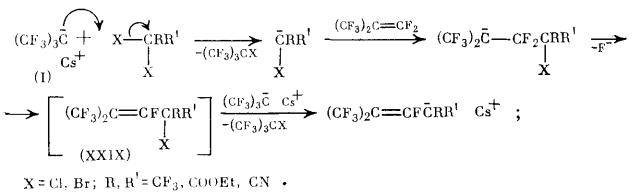
The use of the complex $BF_3.Et_3N$ in the reaction of PFIB with malonic esters made it possible to achieve the preparative synthesis of the allenes (XXVII).[101] This complex not only activates the methylene group but at the same time it plays the role of the dehydrofluorinating agent.

The condensation of PFIB with active methylene groups in the presence of CsF has also been investigated. 3-Ethoxycarbonyl-3-phenyl-1,1-bis(trifluoromethyl)allene was obtained in this way from phenylacetic ester[103]. More reactive allenes, obtained from malonic acid derivatives, have been isolated in the form of stable adducts with CsF:[103]

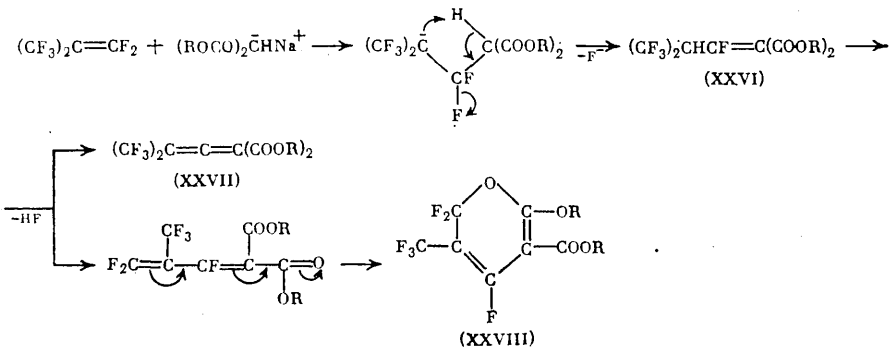


Analogous adducts have been obtained also in the reaction of PFIB with certain compounds containing dihalogenomethylene groups[104]. In this case the attacking species is the α-halogenocarbanion, which is generated as a result of the halogenophilic reaction of the perfluoro-t-butyl anion with a *gem*-dihalide [see Eqn.(14)]. This carbanion substitutes the vinyl fluorine atom in PFIB with formation of the intermediate (XXIX), which is also dehalogenated by the anion (I) (Scheme 19):

Scheme 19



Scheme 18



¶ This rules out the possibility of obtaining the allyl substitution products in aprotic dipolar solvents containing the F^- anion (see the discussion in the communication of Zeifman et al.[87]).

† The condensation of PFIB with sodiomalonodinitrile afforded $(CF_3)_2CHCF=C(CN)_2$.[102]

In the presence of CsF and under comparatively mild conditions, PFIB condenses with acetonitrile to form the salt (XXX):[105]

$$(CF_3)_3\bar{C} \underset{}{\overset{MeCN}{\rightleftharpoons}} (CF_3)_3CH + \bar{C}H_2CN$$

$$(CF_3)_2C{=}CF_2 \xrightarrow[-F^-]{\bar{C}H_2CN} (CF_3)_2C{=}CFCH_2CN \xrightarrow[-(CF_3)_3\bar{C}]{(CF_3)_3\bar{C}}$$

$$\rightarrow (CF_3)_2C{=}CF\bar{C}H{-}CN \xrightarrow[-(CF_3)_3CH]{(CF_3)_2C=CF_2} [(CF_3)_2C{-}CF]_2\bar{C}{-}CN\ Cs^+ \quad .$$

(XXX)

PFIB reacts analogously with acetyl bromide in the presence of CsF.[7]

Vinyl substitution products have been obtained also in the condensation of PFIB with a number of other *C*-nucleophiles [100,106,107] catalysed by the F^- anion or tertiary amines:

$$(CF_3)_2C{=}CF_2 \longrightarrow \begin{cases} \xrightarrow{Me_2CHCOF} Me_2C(COF)CF{=}C(CF_3)_2 \\ \xrightarrow{(CF_3)_2CHCOOEt} (CF_3)_2C(COOEt)CF{=}C(CF_3)_2 \\ \xrightarrow[NaC(COOMe)_2]{Me} (CF_3)_2C{=}CFC(Me)(COOMe)_2 \quad . \end{cases} \qquad (10)$$

A similar product obtained from PFIB and chloroform is dehalogenated under the reaction conditions with formation of dichlorobis(trifluoromethyl)allene (isolated in the form of an adduct with furan):[108,109]

$$(CF_3)_3\bar{C} + H{-}CCl_3 \rightleftharpoons (CF_3)_3CH + \bar{C}Cl_3 ;$$

$$(CF_3)_2C{=}CF_2 \xrightarrow[-F^-]{\bar{C}Cl_3} (CF_3)_2C{=}C(F)C(Cl)_2 \xrightarrow{-[FCl]} (CF_3)_2C{=}C{=}CCl_2 \quad .$$

The reactions of PFIB with fluorocarbanions are described below in Section VI.

Nitroalkanes

The ambident anions of the salts of nitroalkanes attack the double bond in PFIB via the oxygen atom. The subsequent reactions according to Scheme 20 lead to the formation of the dioxazoles (XXXI).[110,111] The key stage of the reaction is apparently the migration of the perfluoroisobutenoxide anion [cf.Eqn.(7)] from the nitrogen atom to the carbon atom in the intermediate *O*-perfluoroisobutenylnitrone ether:

Scheme 20

$$(CF_3)_2C{=}CF_2 + RCH{=}N(O)O^- \rightarrow [(CF_3)_2C{=}CFO{-}N{=}CHR(O)] \rightarrow$$

$$\rightarrow [(CF_3)_2C{=}CF\bar{O}CH{-}N{=}O(R)] \rightarrow [(CF_3)_2C{=}CFOCH{-}N{=}O(R)] \rightarrow$$

$$\rightarrow [(CF_3)_2C{=}CFOC{=}NOH(R)] \xrightarrow{-HF} (CF_3)_2C{-}C(O{-}N)(O{-}C{-}R) \quad .$$

(XXXI)

Phosphorus and Sulphur Ylides

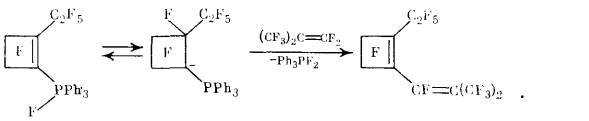
The reaction of PFIB with the ylide (XXXII), leading to the cross-conjugated perfluorotriene (XXXIII),[112,113] has been investigated (for the mechanism, see the review of Tyuleneva et al.[114]):

$$(CF_3)_2C{=}CF_2 + (CF_3)_2C{=}C{=}PPh_3 \xrightarrow{-Ph_3PF_2} (CF_3)_2C{=}C(CF{=}C(CF_3)_2)(CF{=}C(CF_3)_2) \quad .$$

(XXXII) (XXXIII)

When PFIB was allowed to interact with the fluorophosphorane (XXIV), the fluorodiene (XXXVI) was obtained; the preliminary isomerisation of the phosphorane to the phosphorus ylide (XXXV) has been postulated (Scheme 21):[115]

Scheme 21



(XXXIV) (XXXV) (XXXVI)

In the reaction of PFIB with the S-ylide (XXXVII), the intermediate fluorosulphurane is dehydrofluorinated to the fluorine-containing ylide (XXXVIII).[91] As in the reaction of PFIB with α-halogenocarbanions discussed above, in this reaction the only pathway leading to the stabilisation of the intermediate fluorocarbanion involves the elimination of the F^- anion from the CF_2 group and not intramolecular cyclisation (Scheme 22). In this case vinyl substitution is specially preferred owing to the presence of the onium fragment [see Eqn.(8)]:

Scheme 22

$$(CF_3)_2C{=}CF_2 + \underset{(XXXVII)}{Me_2\overset{+}{S}{-}\bar{C}HCOOEt} \rightarrow (CF_3)_2\bar{C}{-}CF(F){-}CH(\overset{+}{S}Me_2)COOEt \rightarrow$$

$$\rightarrow [(CF_3)_2C{=}CF{-}CH(F{-}\overset{+}{S}Me_2)COOEt] \xrightarrow{-HF} \underset{(XXXVIII)}{(CF_3)_2C{=}CF{-}\bar{C}(\overset{+}{S}Me_2){-}COOEt} \quad . \qquad (11)$$

6. Reactions with *P*-Nucleophiles

PFIB readily reacts with trialkyl phosphites, forming trialkoxyfluoroperfluoroisobutenylphosphoranes (XXXIX).[115-117] The synthesis of the adducts (XXXIX) constitutes a rare instance of the isolation of pentacovalent (and not tetracovalent quasi-phosphonium) intermediates of the Arbuzov rearrangement. On heating, the adducts (XXXIX) decompose via two pathways:

$$(CF_3)_2C{=}CF_2 + P(OR)_3 \rightarrow (CF_3)_2C{=}CF{-}PF(OR)_3 \begin{cases} \xrightarrow{-R_2O} (CF_3)_2C{=}CF{-}P(F)(OR)(O) \\ \xrightarrow{-RF} (CF_3)_2C{=}CF{-}P(OR)_2(O) \quad . \end{cases}$$

(XXXIX)

The interaction of PFIB with bis(dialkylamino)chlorophosphines is complicated by the exchange of the substituents at the carbon and phosphorus atoms[118]:

$$(CF_3)_2C{=}CF_2 + ClP(NR_2)_2 \rightarrow (CF_3)_2C{=}C(F){-}PF(NR_2)_2 \rightarrow (CF_3)_2C{=}C(Cl){-}PF_2(NR_2)_2 \quad .$$

PFIB reacts with di-isopropylphosphine to form a vinyl substitution product[119].

The reaction of PFIB with tertiary phosphines is unusual. It does not stop at the stage involving the formation of the vinyl substitution products—fluorophosphoranes $(CF_3)_2C{=}CF{-}PR_3F$; subsequent reactions yielded the perfluorodiene (XL) and the cross-conjugated perfluorotriene (XXXIII)[112,113] (for the reaction mechanism, see Tyuleneva et al.[114]):

$$(CF_3)_2C{=}CF_2 \xrightarrow[-R_3PF_2]{PR_3} (CF_3)_2C{=}CFCF{=}C(CF_3)_2 + (CF_3)_2C{=}C(CF{=}C(CF_3)_2)(CF{=}C(CF_3)_2) \quad .$$

(XL) (XXXIII)

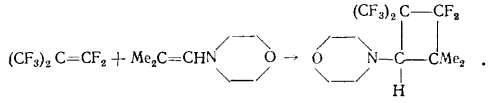
The rate and direction of the reaction depend greatly on the nature of the phosphine and the polarity of the solvent. Thus PFIB reacts with tributylphosphine in ether to form only products of the exchange of the ligands in the intermediate $(CF_3)_2C{=}CFPFBu_3$, namely the phosphoranes $(CF_3)_2C{=}CBuPF_2Bu_2$ and $(CF_3)_2C{=}CFPF_2Bu_2$, while in acetonitrile and diglyme the defluorodimerisation and defluorotrimerisation products are formed[113].

The observed characteristic features made it possible to extend the reaction of tertiary phosphines with PFIB to other fluoro-olefins and to establish it as a method of synthesis of fluorine-containing dienes[120].

7. Cycloaddition

PFIB enters into [2 + 2]-, [2 + 3]-, and [2 + 4]-cycloaddition reactions with various unsaturated compounds to form products with four-, five-, and six-membered rings, the first two types of cycloaddition being most characteristic of this fluoro-alkene. PFIB undergoes the Diels–Alder reaction only under very severe conditions (with cyclopentadiene at 150 °C and with butadiene at 200 °C) and produces a low yield of cyclic 1,4-adducts[121]. On the other hand, a cyclic analogue of PFIB, namely perfluoromethylenecyclopropane, is an active dienophile and forms an adduct with cyclopentadiene at a temperature as low as 0 °C.[122]

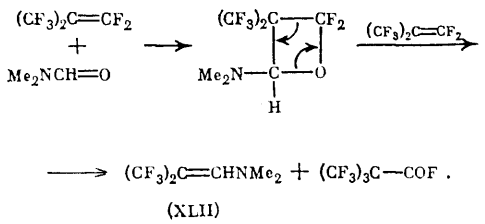
At the same time, PFIB readily undergoes cycloaddition reactions with multiple bonds enhanced nucleophilic properties. Such reactions include the formation of a derivative of cyclobutane when PFIB interacts with isobutenyl-morpholine[123]:



This reaction is accelerated with increase of the polarity of the solvent, which supports an ionic mechanism of the cycloaddition. Perfluoroalkenylation products have been obtained by the interaction of PFIB with the enamine (XLI)[123] or the keten acetal[100] (Scheme 23). Evidently the intermediate dipolar ions are stabilised not only by cyclisation but also by the elimination of the F^- anion and a proton:

PFIB probably reacts with dimethylformamide via the [2 + 2]-cycloaddition mechanism[124], but the unstable cyclic adduct decomposes with elimination of carbonyl fluoride, which leads to the fluoride of perfluoropivalic acid and the enamine (XLII) (Scheme 24):

Scheme 24

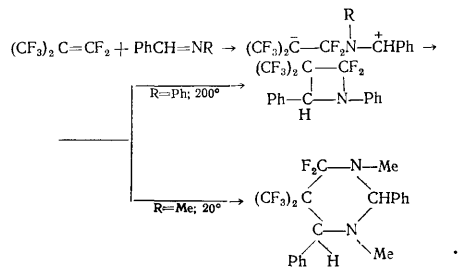


(XLII)

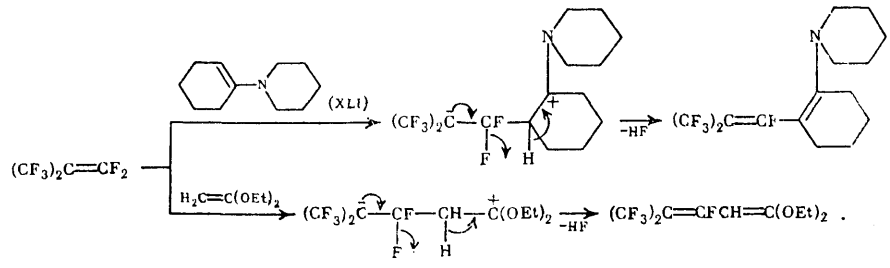
PFIB reacts in the same way with dimethylaminobenzaldehyde#[125], nitrosobenzene[61], and sodium nitrite[61], which lead to the olefin $(CF_3)_2C{=}CHC_6H_4NMe_2$ and the anil and oxime of hexafluoroacetone respectively.

A stable cyclic adduct has been obtained from PFIB and benzylideneaniline under severe conditions. The more nucleophilic benzylidenemethylamine reacts with PFIB much more readily; however, this involves the formation of a six-membered cyclic adduct incorporating two molecules of the imine (Scheme 25)[126]:

Scheme 25



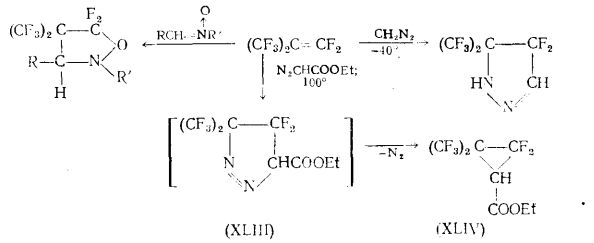
Scheme 23



In the absence of the activating dimethylamino-group, aromatic aldehydes react with PFIB only under the conditions of nucleophilic catalysis[125].

PFIB readily gives rise to 1,3-cycloaddition products on reaction with diazomethane[93] and nitrones[127,128]. Pyrazoline (XLIII) obtained from PFIB and diazoacetic ester eliminates nitrogen, which leads to the cyclopropane (XLIV) (Scheme 26):[91]

Scheme 26



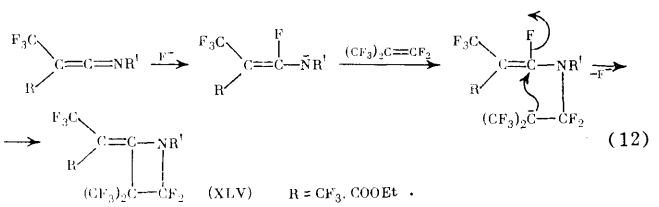
(XLIII) (XLIV)

The range of cycloaddition reactions with participation of PFIB has been expanded by employing nucleophilic catalysts. This approach made it possible to involve in the cycloaddition to PFIB compounds containing electrophilic multiple bonds.

We may note that the application of nucleophilic catalysis is of general importance in the chemistry of compounds with electrophilic multiple bonds and in particular such catalysis is used widely for the dimerisation and trimerisation of isocyanates[129], ketens[130], keten imines[72], and activated olefins[131]. The application of nucleophilic catalysts makes it possible to achieve also mixed cyclodimerisation, for example, in the case of hexafluoroacetone and ketens[132] or isocyanates[133].

In the presence of alkali metal fluorides or tertiary amines, PFIB reacts with fluorine-containing keten imines under mild conditions in accordance with Scheme 27 to form cyclic adducts—the azetidines (XLV).[134] The role of the catalyst evidently consists in converting the electrophilic keten imine into a nucleophilic mesomeric anion capable of adding to the double bond of PFIB. Such addition is accompanied by cyclisation and regeneration of the catalyst:

Scheme 27



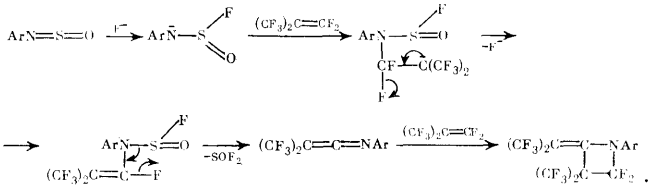
(12)

(XLV) R = CF_3, COOEt.

The azetidines (XLV, R=CF_3) are also formed in the reaction of PFIB with primary amines in the presence of the same catalyst[134], since the keten imines themselves are obtained from PFIB and primary amines [see Eqn.(5)]. It is striking that the rate of addition of RNH_2 to PFIB is higher than the rate of the subsequent reactions, including the formation of imidoyl fluorides and keten imines. By selecting the appropriate reactant ratio and the catalyst, this makes it possible to control the reaction by arresting it at any stage. Such control cannot be achieved in the reaction of PFIB with the weakly basic urethane. In this case the first stage is the slowest and the only product isolated is therefore the corresponding *N*-epoxycarbonylazetidine[134].

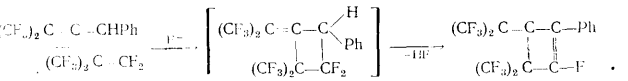
The azetidines (XLV, R=CF_3) are also formed in the reaction of PFIB with *N*-sulphinylamines in the presence of CsF (Scheme 28).[135] Evidently vinyl substitution and β-elimination of SOF_2 and not cycloaddition take place initially in this reaction; the keten imines thus formed combine with a further PFIB molecule:

Scheme 28



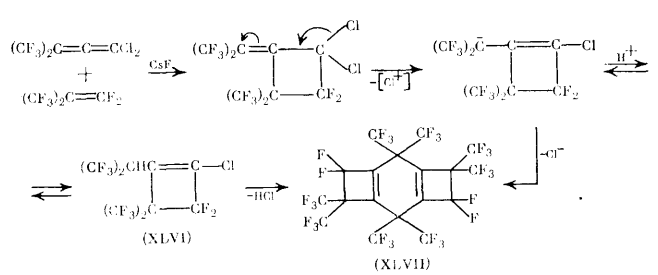
This Scheme confirms that the reaction of PFIB with *N*-sulphenylbenzenesulphonamide leads to *N*-benzenesulphonyl-bis(trifluoromethyl)keten imine, which gives rise to a stable adduct with CsF, analogous to the adduct (XIX).[87]

The application of nucleophilic catalysis also made it possible to achieve the cycloaddition of PFIB to allenes[10]:



PFIB apparently interacts via the analogous Scheme 29 with dichlorobis(trifluoromethyl)allene. The reduction of the intermediate cyclic adduct by the $(CF_3)_3C^-$ anion results in the formation of the cyclobutene derivative (XLVI), whose dehydrochlorination leads to the tricyclic compounds (XLVII):[108,109,136]

Scheme 29



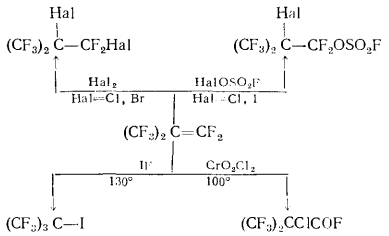
(XLVI) (XLVII)

IV. REACTIONS WITH ELECTROPHILES

As already mentioned above, in reactions with electrophiles PFIB is much less reactive than lower fluoro-olefins and these reactions require as a rule extremely severe conditions.

The addition of halogens to PFIB via a radical mechanism can be achieved photochemically or thermally in the presence of catalysts. Thus PFIB is chlorinated in the gas phase at 128 °C over $FeCl_3$ on activated charcoal (AC).[137] The heat of chlorination of PFIB is ΔH = 42.2 kcal mole^{-1}, while for tetrafluoroethylene ΔH = 57 kcal mole^{-1}. PFIB is not brominated under illumination; the method of elimination of unsaturated impurities from PFIB is based on this property of the latter. However, in the presence of catalytic amounts of acetamide, PFIB combines with bromine under ultraviolet irradiation[10]. The addition of iodine fluoride to PFIB [14] and its reaction with chromyl chloride[138] on heating have also been described.

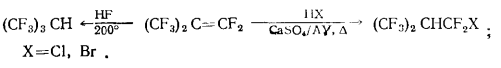
Highly reactive chlorine and iodine fluorosulphates add to PFIB at a temperature as low as 20 °C:[139]



(13)

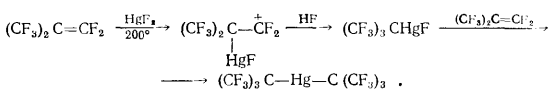
PFIB exchanges fluorine for chlorine under severe conditions on treatment with $AlCl_3$ and, in contrast to the exchange reaction with the Cl^- anion [Eqn.(1)], the polysubstitution products $ClCF_2C(CF_3)=CCl_2$ and $Cl_2FC(CF_3)=CCl_2$ are formed in this case together with monochlorides and dichlorides[25].

The addition of hydrogen halides to PFIB in the gas phase takes place only on heating, in contrast to nucleophilic hydrohalogenation [Eqn.(2)]:[140]



X=Cl, Br .

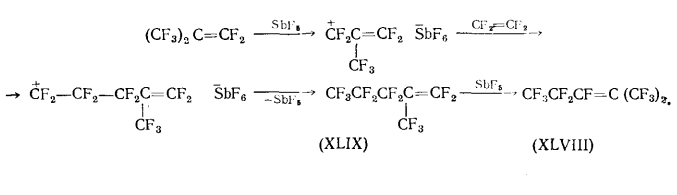
Mercuration of PFIB in anhydrous HF or AsF_3 yields bis-(perfluoro-t-butyl)mercury:



It has been suggested that the reaction proceeds as a result of the attack by the metal cation on the double bond of PFIB or via a four-centre cyclic transition state[141]. The nucleophilic mercuration of PFIB takes place under much milder conditions[7].

In the presence of SbF_5, it is impossible to achieve the interaction of PFIB with elemental sulphur. The attacking agent is apparently the doubly charged sulphur cation formed when sulphur is oxidised by SbF_5.[142] The reaction of PFIB with bis(pentafluorophenyl) disulphide has also been studied[143]:

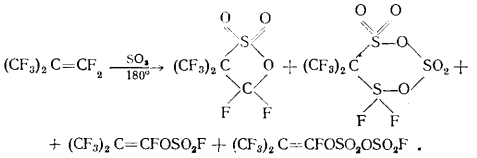
The condensation of PFIB with fluorinated ethylenes has also been achieved in the presence of SbF_5 under extremely mild conditions[144,145]. The primary step in these reactions is the formation of the perfluoromethylallyl cation (detected by ^{19}F NMR):



Together with the 1 : 1 adduct (XLVIII), the 1 : 2 adduct $C_3F_7C(CF_3)=CFC_2F_5$ is formed in the reaction via the intermediate isohexene (XLIX).

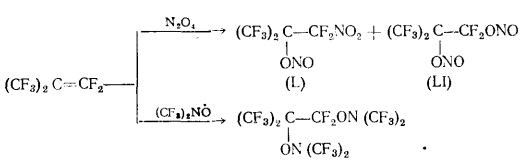
PFIB reacts via an analogous mechanism with perfluoroazapropene, giving rise to a high yield of the perfluoroenamine $(CF_3)_2NCF=C(CF_3)_2$.[146]

The electrophilic addition of sulphur trioxide to PFIB at 180 °C leads to the corresponding β-sultone and pyrosultone together with the products of their further reactions[147]:

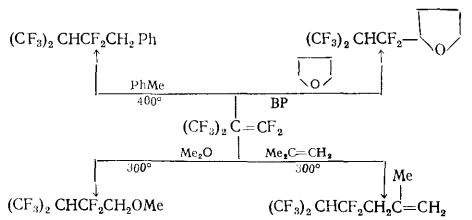


The nitration of PFIB by nitrogen oxides proceeds via a radical mechanism (Scheme 30): approximately equal amounts of the nitronitrite (L) and the dinitrite (LI) were obtained in this reaction[148]. PFIB also combines with bis(trifluoromethyl)amine oxide:[149,150]

Scheme 30

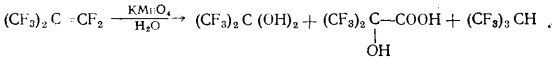


The fluoroalkylation of tetrahydrofuran by PFIB takes place with initiation by benzoyl peroxide (BP).[151] On heating, PFIB is also inserted in the C–H bonds of isobutene, toluene[152], and dimethyl ether[153]:



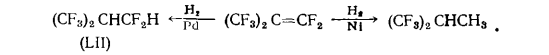
V. OTHER REACTIONS

PFIB is readily oxidised by potassium permanganate in water[10]. This reaction constitutes a convenient laboratory method for the synthesis of hexafluoroacetone[154]. Among its side products, hexafluoro-α-hydroxyisobutyric acid[155] and monohydroperfluoroisobutane[10] were identified:



The formation of hexafluoroacetone has also been established in the reaction of PFIB with sodium nitrite in dimethylformamide[61] and with hydrogen peroxide in aqueous alkali[35]. The interaction of PFIB with fluorine oxide gives rise to the epoxy-derivative of PFIB.[38]

The hydrogenation of PFIB in the presence of a palladium catalyst leads to dihydroperfluoroisobutane (LII) as the only product[56]. When nickel is used, the main hydrogenation product is 1,1,1-trifluoro-2-trifluoromethylpropane[157]:



Traces of dihydroperfluoroisobutane have also been detected in the products of the reaction of PFIB with the Hantzsch ester[23].

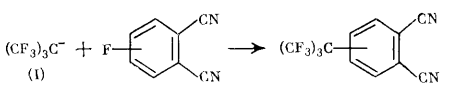
It has been shown that PFIB does not form homopolymers on radical initiation and γ-irradiation. However, the formation of copolymers with certain acrylates on initiation by acetyl peroxide has been noted[158,159]. The copolymer with tetrafluoroethylene, obtained on γ-irradiation, includes 4% of PFIB.[160] Studies of the kinetics of the copolymerisation of PFIB with tetrafluoroethylene have been described by Isamukhamedov et al.[161] and Gafurov et al.[162]

VI. REACTIONS OF THE PERFLUORO-t-BUTYL ANION

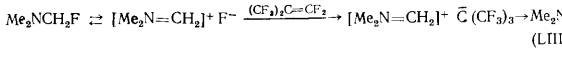
The study of the methods of synthesis and reactions of the perfluoro-t-butyl anion (I) is associated with the possibility of synthesising a wide variety of compounds containing the $(CF_3)_3C$ group and their practical employment. This Section includes the literature on the chemistry of this anion which has not been incorporated in a special review on this topic[7] published in 1976§. It is noteworthy that the chemistry of this anion differs from the chemistry of the primary and secondary fluorocarbanions not only by its wide variety but also by specific features associated with the increased stability of the anion. The anion (I) is a more effective leaving group than, for example, the perfluoroisopropyl anion. The ease of the decarboxylation of $(CF_3)_3C-COOH$ compared with $(CF_3)_2CF-COOH$ [163] and also the instability of perfluoro-t-butylmethanols in alkaline media are consistent with this finding[164].

For the same reasons, certain reactions known for primary and secondary fluorocarbanions cannot be carried out with the anion (I), since in the presence of the F^- anion these reactions are reversible and the equilibrium is displaced towards the initial compounds. This applies to the interaction of the anion (I) with benzoyl chloride[164,165] and dimethylaminotrifluorosulphurane[166]. Furthermore, as a consequence of its reversibility, the dimerisation of PFIB rarely accompanies its reactions initiated by the F^- anion[7]. It is remarkable that the pseudohalogen character of the perfluoro-t-butyl group makes it possible to employ compounds of the type CF_3C-X (X = Br, PhS, etc.) as electrophiles for the bromination, sulphenylation, and other similar reactions involving fluorocarbanions. It is also significant that the anion (I) in solutions is in equilibrium with free PFIB, so that the anionoid intermediates formed in the reactions of the anion (I) frequently interact with PFIB.

The anion (I) has been alkylated by $I(CH_2)_nI$ ($n = 1$ [104] and $n = 3$ or 4 [167]), $ClCH_2SCH_3$,[91] $(ClCH_2)_2O$, and $(ClCH_2)_3N$. The corresponding perfluoro-t-butyl derivative has been obtained from the anion (I) and α-chlorotetrahydrofuran[169]. The synthesis of perfluoro-t-butylphthalonitriles, which have been used to obtain phthalocyanines, has been described[170]:



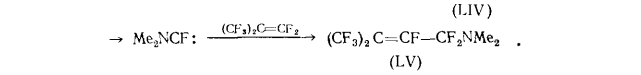
The interaction of PFIB with fluorotrimethylamine leads to the tertiary amine (LIII).[71] The anion (I) is probably formed in this case and the source of the fluoride ion is fluorotrimethylamine itself:



(LIII)

§ Except where stated otherwise, this Section deals with the reactions of the anion (I) generated by the addition of alkali metal fluorides to PFIB.

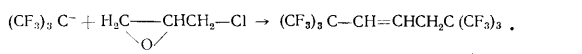
PFIB reacts in an unusual manner with α,α-difluorotrimethylamine. Fluoroamine adds reversibly under these conditions to the fluoro-olefin and compound (LIV) is formed; on heating, it decomposes into monohydroperfluoroisobutane and dimethylaminofluorocarbene, which adds to PFIB to form the amine (LV):[172]



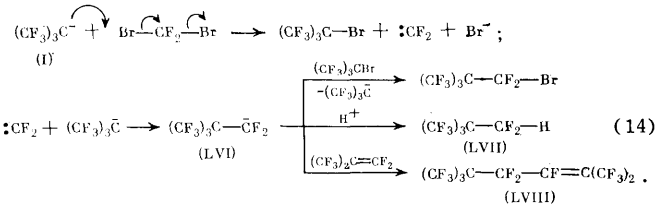
(LIV)

(LV)

When the anion (I) interacts with epichlorohydrin, the opening of the epoxide ring and dehydration are accompanied by the substitution of chlorine by the $(CF_3)_3C$ group[173] (for the description of the mechanism, see Gervits et al.[174]):



The replacement of bromine by the perfluoro-t-butyl group takes place in the reaction of the anion (I) with CF_2Br_2.[175] However, in contrast to the usual alkylation of the anion (I) where the halogen atom undergoes nucleophilic substitution, in this case the interaction proceeds via a completely different mechanism. The anion (I) is initially brominated by CF_2Br_2, which is accompanied by the generation of difluorocarbene to which the anion (I) and bromine are then added in a coupled reaction to form perfluoroneopentyl bromide. The hydride (LVII) and the olefin (LVIII) were detected as side products, which confirms the formation of the carbanionic intermediate (LVI):



(14)

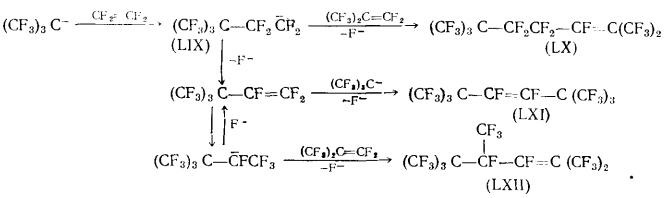
(LVII)

(LVIII)

The reaction of the anion (I) with chlorodifluoromethane, leading to compounds (LVII) and (LVIII), also proceeds via the intermediate formation of difluorocarbene[175]. Substitution of bromine by the $(CF_3)_3C$ group on treatment of $BrCF_2.CF_2Br$ by the anion (I) also proceeds via an elimination–addition mechanism [see Eqn.(15)].

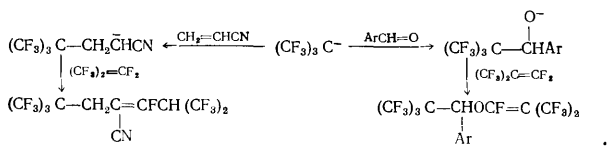
The main product of the reaction of the anion (I) with tetrafluoroethylene is the olefin (LX); the isomers (LXI) and (LXII) are formed together with this compound (Scheme 31)[176]. It is striking that the intermediate carbanion (LIX) is capable of being involved in the reaction with a second PFIB molecule in preference to the usual stabilisation pathway—the β-elimination of the F^- anion:

Scheme 31

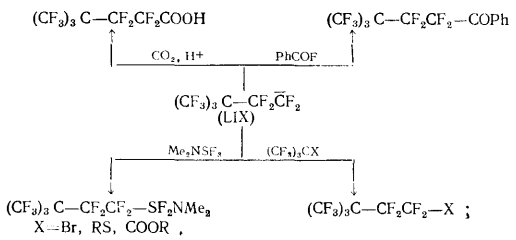


(LIX) (LX) (LXI) (LXII)

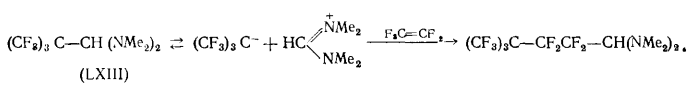
The *C*-anions[177] or *O*-anions[125], generated by the addition of $(CF_3)_3C^-$ to acrylonitrile or aromatic aldehydes respectively, are also capable of subsequent vinyl substitution reactions with PFIB:



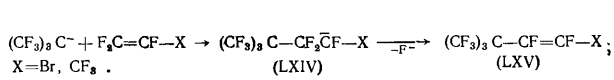
The reactions involving the coupled addition of the anion (I) to tetrafluoroethylene, which include the formation of the olefin (LX), are fairly general. Thus the intermediate carbanion (LIX) adds to the carbonyl group of CO_2 and substitutes the fluorine in benzoyl fluoride or in Me_2NSF_3.[178] It has also been possible to achieve the bromination, sulphenylation, and alkoxycarbonylation of the anion (LIX) in the condensation of PFIB with tetrafluoroethylene in the presence of CsF and compounds of the type of $(CF_3)_3CX$: [178,179]



A characteristic feature of the latter reactions is that the anion (I), participating in the initial stage where the intermediate (LIX) is generated, is liberated in the concluding stage and is not consumed in the reaction. Thus in fact the entire process constitutes the insertion of tetrafluoromethylene in the C–C, C–Br, or C–S bond catalysed by the anion (I). The anion (I) also catalyses the exchange of chlorine for fluorine in the vicinal chlorosulphide, $(CF_3)_2C(SPh)-CF_2Cl$ in its interaction with CsF.[179] Tetrafluoroethylene is also inserted in the C–C bond of the geminal diamine (LXIII) and in this case the addition of the anion (I) is not required, since the initial diamine is capable of dissociating into the anion (I) and the corresponding immonium cation[178]:

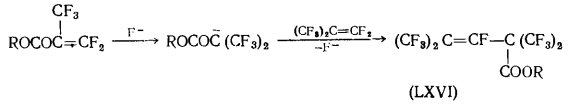


The interaction of the anion (I) with bromotrifluoroethylene[107] or hexafluoropropene[180] leads only to the vinyl substitution products (LXV). The intermediate fluorocarbanion (LXIV) is less reactive than the fluorocarbanion (LIX) and is stabilised only as a result of the β-elimination of the F^- anion:



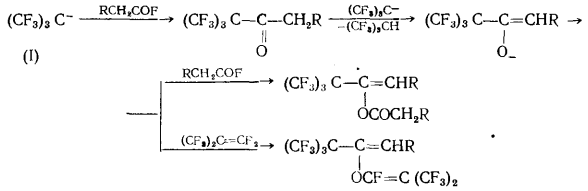
It is of interest to note that, under the conditions of thermodynamic control, the product is not the olefin (LXV, X = CF_3) but its isomer, namely the olefin $(CF_3)_2CFCF=C(CF_3)_2$ resulting from the interaction of PFIB with the perfluoroisopropyl anion[181]. On the other hand, the condensation of PFIB with perfluoroazapropene, catalysed by CsF, results in the formation of $(CF_3)_3C-CF=NCF_3$ regardless of the conditions[182,183].

The interaction of PFIB with perfluoromethacrylic acid esters in the presence of CsF leads to the unsaturated esters (LXVI).[107] In the given case, the reaction is propagated not by the anion (I) but by the C-anion of the hexafluoroisobutyric acid ester, apparently as a consequence of the greater ease of formation of the latter [cf.Eqn.(10)]:



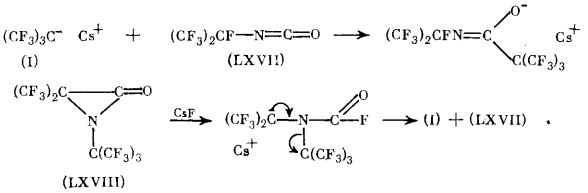
The interaction of the anion (I) with carboxylic acid halides is in general reversible because the carbonyl compounds formed are capable of decomposing in the presence of the F^- anion with reformation of the initial anion (I).[165] The equilibrium position is then determined by the electrophilic properties of the carbonyl carbon atom in the reaction products. Thus the anion (I) is acylated under mild conditions by carbonic acid derivatives[165,184,185]. However, perfluoro-t-butyl phenyl ketone cannot be obtained under the usual conditions of the generation of the anion (I); in this case the reaction equilibrium is fully displaced towards the initial compounds[165]. The benzoylation of the anion (I) has been achieved only using hexamethylguanidinium as the counterion[22].

When the anion (I) is acylated by aliphatic carboxylic acid halides containing an α-hydrogen atom, the equilibrium shifts towards the reaction products, since, on treatment with the anion (I), the intermediate alkyl perfluoro-t-butyl ketones give rise to the corresponding enolates, which are then converted into the *O*-acyl and *O*-perfluoroisobutenyl derivatives[21,186]:

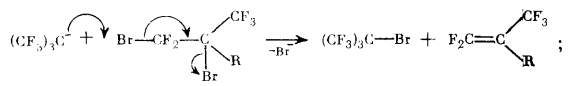


The addition of the anion (I) to the carbonyl group of perfluoroisopropyl isocyanate via Scheme 32 leads to the stable adduct of perfluoropivaloylimine and CsF. It is remarkable that the same adduct is formed when the α-lactam (LXVIII) is treated with CsF. The driving force of the latter reaction is the ease of migration of the perfluoro-t-butyl anion from the nitrogen atom to the carbon atom[187]:

Scheme 32



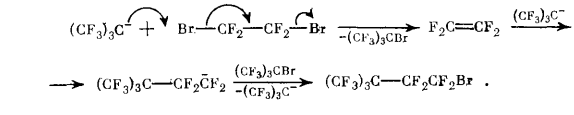
The anion (I) is brominated on treatment with elemental bromine[188]. It is of greater interest that $(CF_3)_3C-Br$ is formed also in the reactions of the anion (I) with certain compounds containing the C–Br bond. They include the *gem*-dibromopolyfluoroalkanes mentioned above. The anion (I) is also brominated when it reacts with vicinal dihalogenopolyfluoroalkanes[107]. The olefins formed together with $(CF_3)_3CBr$ undergo subsequent condensation with PFIB catalysed by the F^- anion:



R=F, COOEt .

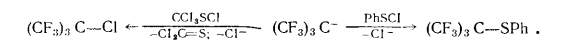
In contrast to those reactions where the anion (I) behaves as a debrominating agent, its interaction with $CF_2BrCHFBr$ leads to the dehydrobromination of the latter[107].

The reaction of the anion (I) with dibromotetrafluoroethane constitutes a special case[107]. As a result of the debromination of the vicinal dibromide by the anion (I), the reaction leads to the formation of perfluoro-t-butyl bromide and tetrafluoroethylene, which reacts further via a coupled nucleophilic addition mechanism:

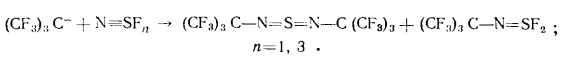


(15)

The anion (I) is smoothly sulphenylated by ethanesulphene, arenesulphene[189–191], and dialkylaminosulphene[189] chlorides. The reaction constitutes a convenient method of synthesis of perfluoroalkyl sulphides and perfluoroalkanesulphenamides. On the other hand, the interaction of the anion (I) with sulphene chlorides having electron-accepting substituents leads only to its chlorination[189]:



Areneselenyl chlorides react with the anion (I) analogously to arenesulphenyl chlorides[191]. Perfluoroalkylation at the nitrogen atom with the aid of the anion (I) was achieved when the latter reacted with thiazyl fluoride and thiazyl trifluoride[192]:



$n=1, 3$.

CF_3COONO has been proposed as the nitrosating agent for the anion (I).[193]

Thus it follows from the data examined that the reactions of the anion (I) constitute a fairly general method of synthesis of compounds containing the $(CF_3)_3C$ group. Certain compounds of this type have been suggested as gas-transferring media[167,194,195] and as monomers for the synthesis of thermostable silicone elastomers[196,197]. Compounds containing the $(CF_3)_3C-CF_2$ group have been synthesised by the reaction of the anion (I) with CF_2Br.[175] Reactions involving the coupled addition of the anion (I) to tetrafluoroethylene have led in their turn to a pathway towards the synthesis of the higher homologues—compounds with the $(CF_3)_3C-CF_2CF_2$ group. These compounds are of interest because they provide a method for the introduction of functional groups into fluoroolefins with a simultaneous increase of the length of their hydrocarbon chains[178].

---o0o---

The data presented in this review show that, in terms of its importance for the chemistry of organofluorine compounds, PFIB is fully comparable with the most important fluoroolefins such as tetrafluoroethylene and hexafluoropropene. Whereas the latter are industrially important and are manufactured on a large scale, PFIB has found extensive applications, despite the limitations associated with its high toxicity, in the laboratory synthesis of functional organofluorine com- of many types. The most important of these include hexafluoroacetone[198], derivatives of α-hydrohexafluoroisobutyric and perfluoromethacrylic acids[33], bis(trifluoromethyl)keten[32] and its imines[72], acetals[199], and aminals[79], allenes[103], and various heterocyclic compounds with *gem*-trifluoromethyl groups.

At the same time PFIB proved to be a convenient model compound for the solution of various problems associated with the nucleophilic reactions of fluoro-olefins such as the relative contributions of addition and vinyl and allyl substitution processes, the application of nucleophilic catalysis in addition and cycloaddition reactions, etc. Thus the development of the chemistry of PFIB has in many respects determined the general advances in the study of fluorine-containing compounds of various types, apart from purely practical results.

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Nesmeyanov Institute of
Organoelemental Compounds,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 462-486 (1984) U.D.C. 547.541

Some Rearrangements of Free Alkyl Radicals and Alkyl Cations in Solutions

O.A.Reutov

The results of studies of rearrangement reactions by the author and his co-workers during the last 20 years are described. A rearrangement of the n-propyl free radical in solutions as a result of the hydrogen 1,3-shift has been discovered and its characteristic features have been investigated (using carbon-14, deuterium, and tritium). The reaction involving the formation of organomercury compounds from mercury salts of carboxylic acids and peroxides has been studied and a mechanism has been proposed for it. New skeletal rearrangements in the thermal decomposition of cycloalkyl peroxides in benzene and bromoform have been discovered. It has been shown by the method of double ^{13}C NMR that some of the reactions involve the formation of species which manifest properties intermediate between those of free radicals and carbonium ions. The mechanism of the thermolysis of peroxides is considered.
The skeletal rearrangements and hydride shifts in the deamination and solvolysis of alicyclic compounds have been studied and a number of rearrangements with 1,2-migration of the halogen and in particular the isomerisation of acyloxybromopropanes in organic solvents, which takes place particularly readily, have been observed.
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I. THE ISOMERISATION OF THE n-PROPYL RADICAL

A quarter of a century ago the available information about the feasibility of the isomerisation of free alkyl radicals under mild conditions in the liquid phase as a result of hydrogen shifts was contradictory. Thus Voevodskii and Mardaleishvili[1] suggested that free radicals (n-propyl, primary isobutyl, and cyclohexyl), formed from the corresponding olefins and atomic hydrogen in the presence of deuterium, isomerise in the gas phase (the hydrogen 1,3-shift) at room temperature. This hypothesis explained the high (up to 50%) degree of deuteriation of the radical recombination products.

On the other hand, Kharasch et al.[2] showed that isomerisation with a change in the skeleton does not occur on decomposition of acyl peroxides in carbon tetrachloride:

$$CH_3-CH_2-CH_2^{\cdot} \rightleftarrows (CH_3)_2CH^{\cdot} .$$

Only n-propyl chloride is formed from butyryl peroxide, while only isopropyl chloride is formed from isobutyryl peroxide.

The possibility of the isomerisation of alkyl radicals in liquid-phase photochlorination has been studied[3]. Using deuterium-labelled isobutane, it was shown that the primary isobutyl radical does not isomerise to the tertiary radical:

$$CH_3-CD(CH_3)-CH_2^{\cdot} \rightleftarrows CH_3\dot{C}(CH_3)-CH_2D .$$

Model reactions in which the hydrogen 1,3-shift in the free radical formed initially should be thermodynamically favourable, i.e. should lead to the formation of more stable radicals, have been investigated[4-7]. However, the n-hexyl as well as the δ- and γ-phenylalkyl radicals did not isomerise. Only the non-isomerised chlorides were formed in all cases:

$$(CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-COO)_2 \xrightarrow{CCl_4} \longrightarrow CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-Cl ;$$

$$(Ph-CH_2-CH_2-CH_2-CH_2-COO)_2 \xrightarrow{CCl_4} Ph-CH_2-CH_2-CH_2-CH_2-Cl ;$$

$$(Ph-CH_2-CH_2-C(CH_3)H-COO)_2 \xrightarrow{CCl_4} Ph-CH_2-CH_2-CHCl-CH_3 .$$

However, we believe it to be extremely improbable that the free alkyl radicals, if such are formed as kinetically independent species, for example, in the decomposition of acyl peroxides in solutions, should be altogether incapable of isomerisation. It is well known that free radicals are capable of abstracting a hydrogen atom from the solvent molecule in solutions:

$$R^{\cdot} + H:C\swarrow\searrow \longrightarrow R-H + {}^{\cdot}C\swarrow\searrow .$$

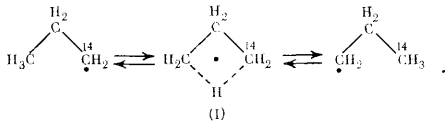
There are no grounds for the assumption that in the presence of suitable steric conditions they cannot abstract hydrogen from their C–H group with a corresponding shift of the free valence. The degree of isomerisation of the radical depends on the ratio of the rates of isomerisation and substitution. It is to be expected that at moderate temperatures the degree of isomerisation is low and isomerisation can be detected only by highly sensitive experimental techniques.

We investigated the decomposition of n-butyryl peroxide, labelled with ^{14}C in the α-position, in boiling carbon tetrachloride[8,9]:

$$(CH_3-CH_2-{}^{14}CH_2-COO)_2 + 2CCl_4 \rightarrow 2CH_3-CH_2-{}^{14}CH_2-Cl + 2CO_2 + CCl_3-CCl_3 .$$

Analysis of the distribution of the radioactive label in propyl chloride showed that, together with the normal product ($CH_3-CH_2-{}^{14}CH_2-Cl$), an appreciable amount (4.0 ± 0.5%) of propyl chloride containing the label in the 3-position ($^{14}CH_3-CH_2-CH_2-Cl$) is formed.

It is more likely that the isomerisation proceeds in a single stage via the four-membered cyclic transition state (I):



(I)

In the light of the results of the study of the isomerisation of the n-propyl radical in solution, it was of interest to consider the reason for the absence of isomerisation in the experiments of De Tar and co-workers[4-6] even when the hydrogen 1,3-shift could lead to a thermodynamically more stable radical of the benzyl type:

$$Ph-CH_2-CH_2-\dot{C}H-CH_3 \rightleftarrows Ph-\dot{C}H-CH_2-CH_2-CH_3 .$$

The author of this review can so far see no reasons, other than the high symmetry of the cyclic transition state in the case of the n-propyl radical, which may favour the 1,3-isomerisation.

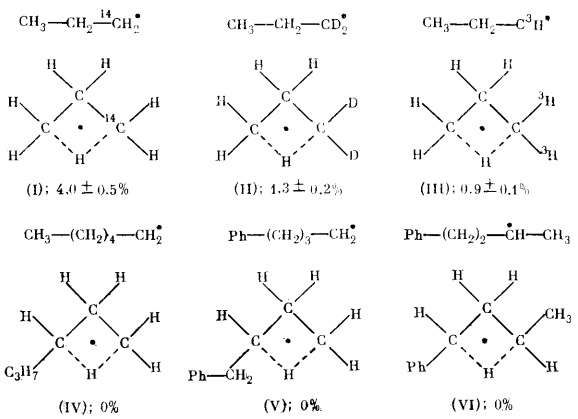
Even a slight decrease of the degree of symmetry in the transition stage (I) appreciably reduces the degree of 1,3-isomerisation. Thus the substitution of two hydrogen atoms even for deuterium {decomposition of [α-D_2]butyryl peroxide in carbon tetrachloride} reduces the extent of isomerisation from 4.0 ± 0.5% to 1.3 ± 0.1%:[10]

$$CH_3-CH_2-\dot{C}D_2 \rightleftarrows \dot{C}H_2-CH_2-CD_2H .$$

If tritium is employed instead of deuterium, the extent of isomerisation falls to 0.9 ± 0.1%.[11]

The proposed transition states for the β-isomerisation of the three free radicals (I)–(II) which we investigated and the free radicals (IV)–(VI) studied by De Tar and co-workers[4,5] are presented in Scheme 1.

Scheme 1



Since the free radical formed in solution can undergo two competing kinds of reactions—can abstract an atom from the solvent molecule or can isomerise—then naturally the faster the former process the lower the degree of isomerisation of the radical. It is known that the ease of abstraction of H, Cl, and Br atoms from the solvent molecule by the free radical increases in the sequence Cl < H < Br. Presumably, when CCl_4 is replaced by bromoform, the degree of isomerisation falls. This hypothesis has been confirmed in the study of the decomposition of [α-D_2]butyryl peroxide in bromoform. In chloroform the radical $CH_3-CH_2-\dot{C}D_2$ isomerised to the extent of 1.3 ± 0.1% and in bromoform only to the extent of 0.7 ± 0.1%.[12]

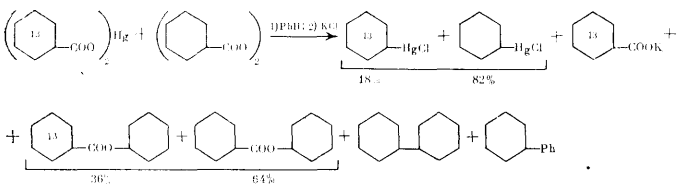
II. THE REACTIONS OF THE MERCURY SALTS OF CYCLOALKANECARBOXYLIC ACIDS WITH PEROXIDES

The reaction of the mercury salts of carboxylic acids with peroxides, leading to the formation of organomercury compounds, has been known for a long time[13]:

$$(R-COO)_2Hg \xrightarrow{(RCOO)_2} R-HgOCOR + CO_2 .$$

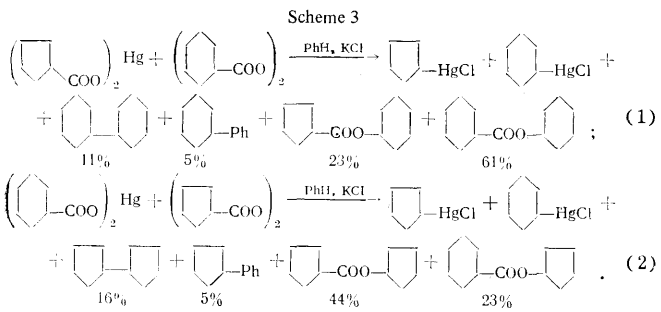
It was believed that the peroxide plays the role of a catalyst in this reaction. In reality the reaction mechanism proved to be more complex[14-16]. The study of the reaction between mercury cyclohexanoate labelled with ^{13}C in the ring and cyclohexanoyl peroxide established[14] that the peroxide is the source of the main product (Scheme 2):

Scheme 2



Since the results obtained were unexpected, we investigated additionally the[15] interactions of mercury cyclopentanoate with cyclohexanoyl peroxide [reaction (1)] and of mercury cyclohexanoate with cyclopentanoyl peroxide [reaction (2)]; both reactions were carried out in benzene at 80 °C under the conditions described by Shatkina et al.[14] The organomercury compounds obtained were converted into the corresponding bromides by the reaction with bromine in glacial acetic acid; the composition of the reaction products was determined by gas–liquid chromatography (GLC). The analytical data for the products formed in the reactions investigated are presented in Scheme 3 and in Table 1:

Scheme 3



It follows from Schemes 2 and 3 that hydrocarbons, namely bicycloalkyls and phenylcycloalkanes, are formed only from the alkyl groups in the corresponding peroxides: bicyclohexyl and phenylcyclohexane in reaction (1) and bicyclopentyl and phenylcyclopentane in reaction (2). The study of the mixture of esters showed that two esters are formed in each reaction, the alcohol component of which corresponds to the alkyl group of the peroxide employed while the acid component corresponds to the alkyl group of the peroxide or the mercury salt.

Table 1 shows that cyclohexylmercury chloride predominates in the mixture of organomercury compounds in reaction (1), which is consistent with the results obtained using mercury [^{13}C]cyclohexanoate.[14] However, cyclohexylmercury chloride also predominates in reaction (2), where the preferential formation of cyclopentylmercury chloride would have been expected by analogy.

Table 1. The composition in reactions (1) and (2) (%) (bromide fraction)*.

Reaction		
(1)	95	5
(2)	73	27

*Bromobenzene was detected in the mixture of bromide in both reactions.

Consideration of the results obtained by Shatkina et al.[14] suggests that two reactions predominate in the system investigated (mercury salts–peroxide): thermal decomposition of the peroxide leading to hydrocarbons and an ester and the reaction of the peroxide with the mercury salt. The latter probably begins with attack by the alkyl group of the peroxide on the mercury atom and the subsequent course of the reaction is determined by the ease of decomposition of the carboxylate radicals formed:



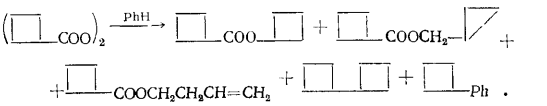
According to Ol'dekop et al.[16] and Hart and Wyman[17], cyclohexanoyl peroxide decomposes faster than cyclopentanoyl peroxide. This can in fact account for the preferential formation of cyclohexylmercury chloride in both reactions. Since there is an excess of cycloalkyl radicals derived from the peroxide in the reaction mixture, the carboxylate radicals formed recombine with them to produce two esters.

The absence from the products of both reactions of hydrocarbons containing the group derived from the mercury salt and also of esters containing the group derived from the mercury salt in the alcohol component suggests that the decarboxylation of the carboxylate radicals takes place in the complex of the mercury salt with the peroxide and is accompanied by a synchronous attack by the cycloalkyl radicals formed on the mercury atom.

III. THERMAL DECOMPOSITION OF ACYL PEROXIDES

The study of the reaction of mercury cyclobutanoate with cyclobutanoyl peroxide in boiling benzene established[18] the formation, together with other products, of esters whose alcohol component has been to a large extent rearranged as a result of the contraction or opening of the ring.

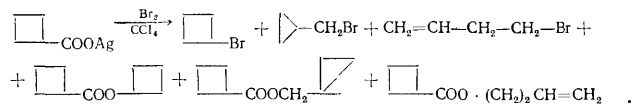
Subsequently a study was made[19] of the thermal decomposition of pure cyclobutanoyl peroxide in boiling benzene. The composition of the reaction products was determined by GLC. The esters were analysed by the chromatography of the reaction mixture and repeated chromatography of the alcohols obtained as a result of the alkaline hydrolysis of the ester fraction. This demonstrated the formation (apart from the cyclobutyl ester of cyclobutanecarboxylic acid) of rearranged esters, namely the cyclopropylmethyl and 3-butenyl esters of cyclobutanecarboxylic acid (the proportions of the products were 47 : 48 : 5). The hydrocarbons in the low-boiling fraction formed in the reaction were not investigated; the formation of bicyclobutyl and phenylcyclobutane was established:



Interesting results were obtained in the study of the thermal decomposition of cyclobutanoyl peroxide in bromoform[20].

In the literature there is a widely held view that the absence of the rearrangement is evidence for a free-radical mechanism and, conversely, that the presence of rearranged products indicates a carbonium ion mechanism. Thus a free-radical mechanism, based mainly on the absence of rearrangement products, has been proposed in studies[21,22] devoted to problems of the halogenodecarboxylation of acids by $Pb(OAc)_4$ and LiCl. In the catalytic decomposition of peroxides by copper complexes[23], the carbonium ion formed by the one-electron oxidation of the free radicals is believed to be responsible for the formation of the rearranged products.

However, we showed[24] that rearranged bromides, namely cyclopropylmethyl and allylmethyl bromides, are formed in the reaction of silver cyclobutanecarboxylate with bromine (the Borodin–Hunsdiecker reaction) in addition to cyclobutyl bromide and the rearranged esters of cyclobutanecarboxylic acid (known from literature data[25]):



It might have been hoped that the analogous rearrangement would be observed also in the thermal decomposition of cyclobutanoyl peroxide. Indeed cyclobutyl bromide and rearranged bromides, namely cyclopropylmethyl and allymethyl bromides, in proportions of 85 : 5 : 10 on average, as well as a mixture of esters, namely cyclobutyl, cyclopropylmethyl, and 3-butenyl esters of cyclobutanecarboxylic acid in proportions of 65 : 30 : 5, were isolated on decomposition of this peroxide in bromoform at 140 °C. Thus a rearrangement, which is fairly likely to have a free-radical mechanism, has been observed[20].

A study has also been made of the problem of the possible formation of rearranged esters in the thermal decomposition of cycloalkylacetyl peroxides. According to Hart and Wyman[26,27], ring expansion products are not formed in the decomposition of aliphatic cyclic acyl peroxides (ranging from C_3 to C_6) in CCl_4. Such compounds have not been detected either in the products of the reaction of cyclobutylmethyl iodide with benzoyl peroxide or di(t-butyl) peroxide or in the reaction of cyclobutylmethyl chloride with Ph_3SnH.[28] Products formed as a result of ring opening have been isolated in the former reaction (the formation of 5-iodopentene has been demonstrated).

We detected[29] rearranged esters in the thermal decomposition of cyclobutylacetyl and cyclopentylacetyl peroxides in benzene at 80 °C. The composition of the main reaction products (esters and high-boiling hydrocarbons) was determined by GLC; the hydrocarbons in the low-boiling fraction were not investigated. The formation of 1,2-dicyclobutyl- and 1,2-dicyclopentyl-ethanes, benzylcyclobutane, and benzylcyclopentane was established. The

esters were analysed by chromatographing the alcohols obtained by the alkaline hydrolysis of the ester fraction; the composition of the esters is presented in Table 2.

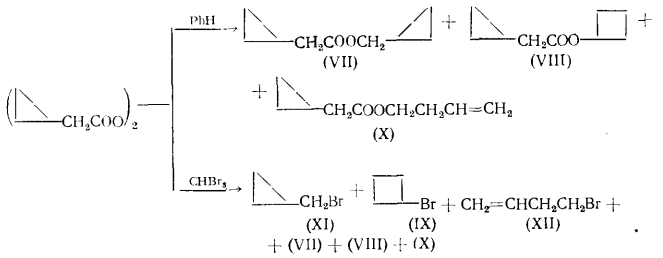
The data in Table 2 show that, apart from esters having the usual structure, esters whose alcohol component has rearranged as a result of ring expansion are formed in the thermolysis of cyclobutylacetyl and cyclopentylacetyl peroxides, the tendency towards ring expansion being more pronounced in the case of cyclobutylacetyl peroxide.

Table 2.

Initial peroxide	Composition of ester fraction	
$[(CH_2)_n CHCH_2COO]_2$	$(CH_2)_n CHCH_2COOCH_2 \cdot CH(CH_2)_n$	$(CH_2)_n CHCH_2 \cdot COOCH(CH_2)_{n+1}$
$n=3$	70	30
$n=4$	80	20

In the study of the thermal decomposition of bis(cyclopropylacetyl) peroxide[26,30], only the cyclopropylmethyl ester of cyclopropylacetic acid (VII) was found in the reaction products. After the decomposition of this peroxide in hexachloroacetone, cyclopropylmethyl chloride and the product of the homoallyl rearrangement of the cyclopropylmethyl radical, namely 3-butenyl chloride, were detected in addition to the ester (VII).[31]

In the study of the thermal decomposition of cyclopropylacetyl peroxide in $CHBr_3$ and in benzene at 65–70 °C [32] we observed for the first time the formation of the products of a rearrangement with ring expansion—cyclobutyl cyclopropylacetate (VIII) and cyclobutyl bromide (IX). Apart from compounds (VIII) and (X), cyclopropyl cyclopropylacetate, 3-butenyl cyclopropylacetate (X), cyclopropylmethyl bromide (XI), and 3-butenyl bromide (XII) are formed in $CHBr_3$; a mixture of the esters (VII) and (VIII) is produced in benzene. The bromides (IX), (XI), and (XII) are obtained in proportions of 7 : 84 : 9, while the esters (VII), (VIII), and (X) are formed in proportions of 80 : 19 : 1 in $CHBr_3$ and 70 : 13 : 17 in benzene:



The compositions and structures of the products were determined by GLC and ^1H NMR.

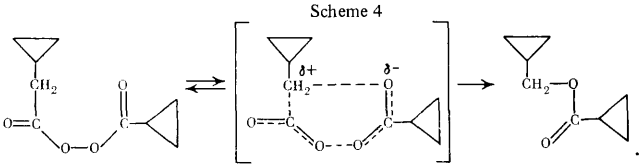
IV. THE MECHANISM OF THE THERMOLYSIS OF ALICYCLIC ACYL PEROXIDES

Analysis of the literature data shows that the thermal decomposition of acyl peroxides is a complex process; the products may be formed via both radical and non-radical (ionic or molecular) mechanisms. The contribution of each pathway depends on the structure of the peroxide and on the conditions of its decomposition.

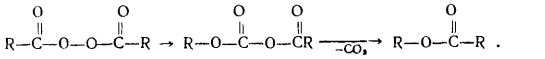
Whereas there is at present no doubt about the radical pathway for the formation of hydrocarbons and halogenoderivatives in the decomposition of acyl peroxide, the mechanism of the formation of esters cannot be decided unambiguously in most cases. The employment of various investigators of the tracer atom (^{18}O) method[30,33] and of the method of optically active peroxides[34], the study of the influence of solvents[35] and polar additives[36] on the decomposition of peroxides, and investigation of the thermolysis kinetics[26] do not as a rule justify a conclusion concerning the true mechanism of the formation of the esters.

In their study of the kinetics of the decomposition of alicyclic peroxides in CCl_4, Hart and Wyman[26] concluded, on the basis of the observed anomalously high rate of decomposition of cyclopropylacetyl peroxide, that the formation of the corresponding ester has a cyclic mechanism (Scheme 4):

Scheme 4



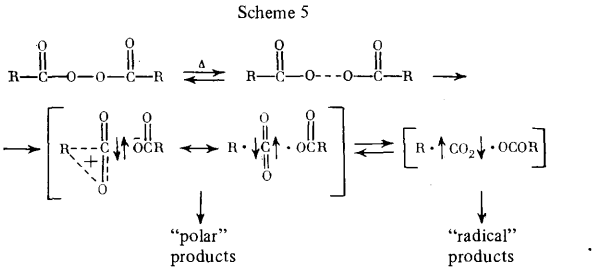
Oae et al.[30], who investigated the decomposition in CCl_4 of the same peroxide labelled with ^{18}O in the carbonyl group, found the complete distribution of the label with respect to both oxygen atoms in the ester and concluded that the ester is formed via a radical pathway. Some investigators[37,38] believe that the esters are the products of the decomposition of the carbonates formed initially:



An ionic mechanism of the decomposition of certain peroxides in polar solvents has been proposed in a number of studies: $RCOO^- {}^+OOCR$ (see, for example, Smid et al.[35]).

Another approach to the explanation of the mechanism of the thermolysis of acyl peroxides has been proposed by Walling[32]. According to Walling's mechanism (Scheme 5), the decomposition of acyl peroxides does not involve competing heterolytic and homolytic reactions, the "polar" and "radical" products being formed from a single intermediate radical-ion pair:

Scheme 5

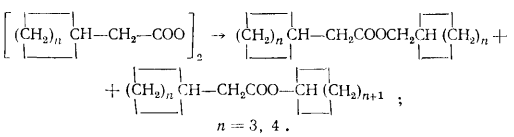


However, this scheme does not allow an objective solution of the problem of the pathway followed in the formation of particular products in these reactions. Thus Walling believes that there are "polar" products, while other investigators[40] who used Walling's mechanism, assigned them to "radical" products.

The method of chemically induced dynamic nuclear polarisation (CIDNP) now makes it possible to draw reliable inferences about the mechanism of the decomposition of acyl peroxides. The polarisation of esters is direct evidence for

the radical pathway leading to their formation on decomposition of acetyl, benzoyl, cyclopropanoyl, etc. peroxides[41]. In other cases the problem of the mechanism of the formation of esters can be solved only tentatively.

In the study of the thermal decomposition of alicyclic acyl peroxides, the formation of rearranged esters was demonstrated[42]. Thus the decomposition of cyclobutylacetyl and cyclopentylacetyl peroxides in benzene involves the formation, apart from esters having the normal structure (cyclobutylmethyl cyclobutylacetate and cyclopentylmethyl cyclopentylacetate respectively), of products rearranged as a result of ring expansion—cyclopentyl cyclobutylacetate and cyclohexyl cyclopentylacetate respectively:

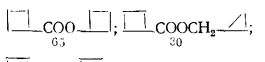
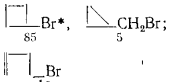
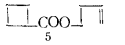
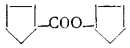
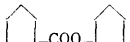
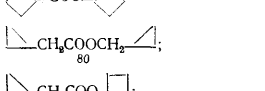
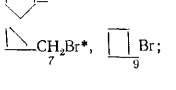
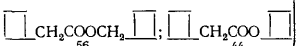
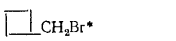
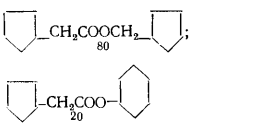
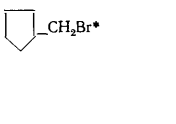


$n = 3, 4.$

The formation of products rearranged as a result of the contraction or opening of the ring, both esters and bromides, was also observed in a study of the thermal decomposition of cyclobutanoyl peroxide in benzene and bromoform[19].

Lippmaa et al.[43] investigated the CIDNP in the thermal decomposition of primary and secondary peroxides in benzene and in a benzene + bromoform mixture, namely cyclobutanoyl peroxide (XIII), cyclopentanoyl peroxide (XI), cyclohexanoyl peroxide (XV), cyclopropylacetyl peroxide (XVI), cyclobutylacetyl peroxide (XVII), and cyclopentylacetyl peroxide (XVIII). According to Kaptein[44], who studied the CIDNP of the decomposition products of the peroxides (XIII)–(XVIII) in hexachloroacetone, cyclo-olefins and cycloalkyl chlorides are polarised, while the esters formed are not polarised; he did not detect rearranged products on decomposition of the peroxides (XIII) and (XVI).

Table 3. Products of the thermolysis of alicyclic acyl peroxides in $CHBr_3$.

Peroxide	Reaction products, rel.%	
	esters	bromo-derivatives
(XIII)		
		
(XIV)		
(XV)		
(XVI)		
(XVII)		
(XVIII)		

*Polarised products.

Lippmaa et al.[43] were interested primarily in the possibility of detecting the CIDNP in the rearranged products. The peroxides were thermolysed at 60–75 °C in the thermostatted cavity of an NMR spectrometer. The authors used 10% solutions of the peroxides in benzene and the same solutions with added 10% $CHBr_3$. Table 3 presents the main products of the decomposition reactions of the peroxides in bromoform (the same mixtures of esters are formed in benzene). Our results[43] of the study of CIDNP in the decomposition reactions of the peroxides (XIII)–(XV) are generally identical with those of Kaptein[44]: only cyclo-olefins and the corresponding bromides with a normal structure are polarised. The rearranged bromides and esters formed on thermolysis of the peroxide (XVII), which we detected, are not polarised.

The thermolysis of the peroxides (XVI) and (XVII) is characterised by the formation of polarised unsaturated hydrocarbons (butene and pentene) and polarised bromides. The character of the polarisation of the hydrocarbons is consistent with the polarisation of the radical before ring opening. In the thermolysis of the peroxide (XVIII), an unsaturated hydrocarbon (hexene) is not formed, which is consistent with the greater thermodynamic stability of the five-membered ring. In the decomposition of the peroxide (XVI) in the benzene + bromoform mixture, 4-bromobutene—the product of the rearrangement of cyclopropylmethyl bromide—is polarised, while the esters formed are not polarised.

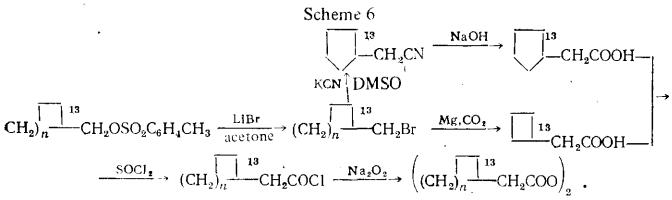
Our results and the literature data permit the conclusion that the CIDNP of esters is observed only in those cases where the decomposition of the peroxide results in the formation of comparatively long-lived radicals. In the remaining cases the absence of the polarisation of the esters can be explained by the fact that the latter are formed via a non-radical (polar) mechanism; or the decomposition of the peroxide proceeds via a radical pathway but there is no appreciable polarisation in the pairs of radicals RCOOR formed in view of the very short (less than 10^{-10} s) existence of the primary cage.

The lack of direct evidence for the free-radical pathway to the formation of esters (rearranged and non-rearranged) led us to test the possibility of the formation of the latter via a heterolytic mechanism[45]. It is known that skeletel rearrangements of alicyclic carbonium ions, formed in nucleophilic substitution reactions (deamination, solvolysis, transformation of alcohols into alkyl halides, etc.), which lead to ring expansion, are always accompanied by the migration of hydride ions in the ring[46–48]. If analogous carbonium ions are formed in the peroxide decomposition reactions which we investigated, one may expect isomerisation as a result of the migration of hydride ions in the expanded ester ring. The use of cycloalkylacetyl peroxides labelled with ^{13}C should show whether hydride shifts leading to the distribution of the ^{13}C atoms in the ring occur in the expanded ring†.

†The use of the ^{14}C label for the investigation of the mechanisms of organic reactions suffers from the significant disadvantage that the distribution of the label in the reaction products is determined by a very laborious degradation, which requires a long time (weeks and even months). Together with Lippmaa, the present author developed for the first time and used[72,73] a new method for the investigation of the rearrangements, consisting of the employment of the ^{13}C label and ^{13}C double nuclear magnetic resonance (DNMR). This method permits an enormous saving of time, since it does not require the degradation of the products; the distribution of the label in the final products is determined from the spectra in the course of several hours. At the present time this is the usual research technique generally accepted throughout the world.

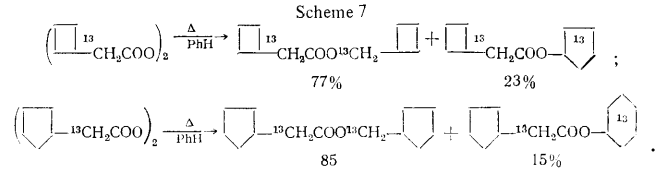
The initial cyclobutyl- and cyclopentyl-[^{13}C]acetyl peroxides were obtained in accordance with Scheme 6#:

Scheme 6



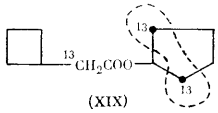
All the stages of the synthesis were tested to make sure that the position of the ^{13}C label is rigorously fixed. The peroxides were decomposed in benzene under the usual conditions[29]. The composition of the ester fraction was determined by GLC; the results of the analysis are presented in Scheme 7:

Scheme 7



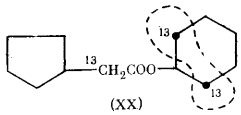
The position of the ^{13}C label in the esters was determined by the ^{13}C double nuclear magnetic resonance; the following distribution of the ^{13}C atoms was found from the spectra:

(a) in the decomposition of cyclobutyl[^{13}C]acetyl peroxide:



(XIX)

(b) in the decomposition of cyclopentyl[^{13}C]acetyl peroxide§:



(XX)

Evidently the alcohol components of both esters contain ^{13}C atoms (in equal amounts) only in the 2,5-positions in compound (XIX) and in the 2,6-positions in compound (XX), as should have been the case in the absence of ring isomerisation. In the cyclobutylmethyl and cyclopentylmethyl components of the corresponding esters, the entire ^{13}C is contained in the methylene group of the side chain.

Thus it has been established that *the esters formed in the thermolysis of cyclobutylacetyl and cyclopentylacetyl peroxides in benzene undergo a skeletal rearrangement leading to the expansion of the ring in the alcohol component of the molecule; there are no hydride shifts.*

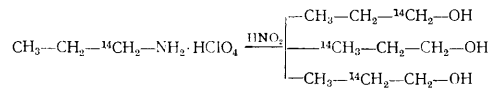
It is known that esters are not formed at all in the photolysis of cyclopentylacetyl peroxide where the most favourable conditions are generated for radical reactions[49]. Taking this fact into account and also our data showing the absence of chemically induced dynamic nuclear polarisation in the esters and the presence of rearranged esters in the thermolysis of the peroxides, one may conclude that the free-radical pathway to the formation of the esters is unlikely. On the other hand, the absence of hydride shifts in the ring in the alcohol components of the rearranged esters rules out the possibility of the formation of at least the usual carbonium ions during the reaction.

The results obtained suggest that the thermolysis of cycloalkylacetyl peroxides involves the formation in the transition state of a radical-ion pair in which species of the carbonium ion type undergo a skeletal rearrangement but do not possess sufficient energy and a sufficiently long lifetime for the occurrence of hydride shifts.

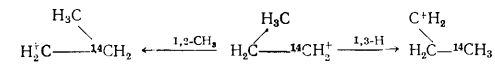
In other words, we encountered in these reactions species which are apparently intermediate between free radicals and carbonium ions.

V. THE ISOMERISATION OF CARBONIUM IONS IN DEAMINATION REACTIONS

In a series of studies[50-56] it was shown that the deamination of n-propylamine labelled with ^{14}C in the 1-position results in the formation of n-propyl alcohol containing ^{14}C (3–4% overall) not only in the 1-position but also in the 2- and 3-positions:



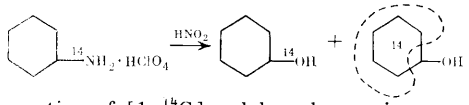
This result was explained either by the intermediate formation of an asymmetrically protonated cyclopropane or by the fact that two parallel reactions of the propyl cation take place: the 1,2-migration of the methyl group and the hydride 1,3-shift:[57]



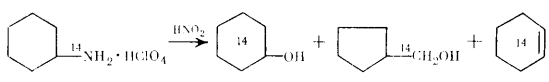
Neither of these explanations can be regarded at the present time as fully justified experimentally.

VI. THE HYDRIDE SHIFTS IN THE DEAMINATION REACTIONS OF ALICYCLIC AMINES

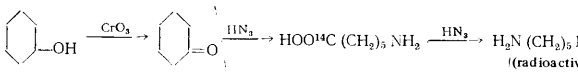
The study of the isomerisation of alkyl cations with migration of hydride ions[51,52,58] led to the hypothesis[51] that the hydroxy-group in the cyclohexanol molecules, formed on treatment of cyclohexylamine with nitrous acid, is not linked solely to the carbon atom to which the amino-group was attached in the initial cyclohexylamine molecule. This was confirmed in another investigation[59] with the aid of the radioactive ^{14}C label:



The interaction of [1-^{14}C]cyclohexylammonium perchlorate with nitrous acid leads to the formation of a mixture of cyclohexanol and cyclopentylmethanol:



In order to establish the position of the ^{14}C atom in the cyclohexanol molecule, the latter was subjected to degradation:



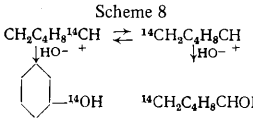
#The initial tosylates were obtained analogously[44].

§The same result was obtained when the ^{13}C DNMR spectra of the alcohols (cyclopentanol and cyclohexanol), isolated after the alkaline hydrolysis of the mixture of esters, were measured.

The pentamethylenediamine proved to be radioactive¶, its radioactivity amounting to 3.7 ± 0.3% of that of the cyclohexanone. This implies that the hydroxy-group in certain cyclohexanol molecules is not linked to the carbon atom to which the amino-group had been attached in the initial cyclohexylamine molecule.

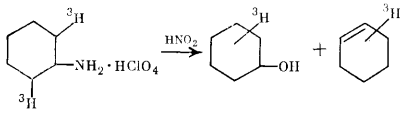
Thus the cyclohexyl cation isomerises in accordance with Scheme 8:

Scheme 8



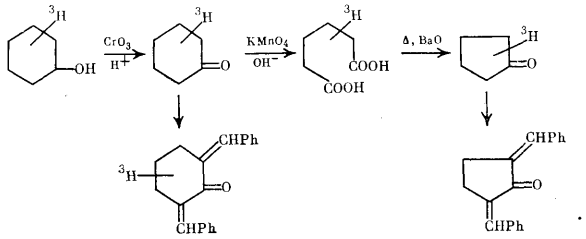
After the study of Reutov and Shatkina[59], it became clear that the mechanism of the Dem'yanov interconversion of alicyclic compounds is more complex than had been thought; *it is complicated by isomerisations involving a shift of hydride ions*.

The isomerisation of the cyclohexyl cation, formed on deamination, as a result of the hydride shift has been confirmed[61] using the tritium label. The products of the deamination of [2,6-^{3}H$_2$]cyclohexylamine are cyclohexene and cyclohexanol:



The degradation of [^{3}H]cyclohexanol was carried out in accordance with Scheme 9:

Scheme 9

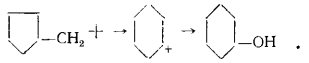


It was established that the extent of isomerisation of the cyclohexyl cation is 4.8 ± 0.3% and that the isomerisation is mainly due to the H$^-$1,2-shift (3.5%): the contribution of the H$^-$1,3-shift was 1.3% in this instance.

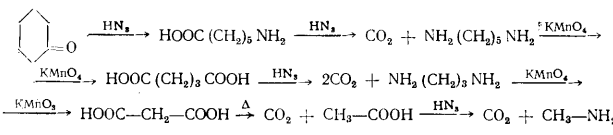
The hydride shift accompanying the expansion of the five-membered ring on deamination of [1-^{3}H]cyclopentylmethylamine have been investigated by the present author and his co-workers in Ref.62 and the isomerisation in the deamination of n-alkylamines has been studied in Refs.63–65.

The influence of anions with different nucleophilic properties on the degree of isomerisation of the [1-^{14}C]cyclohexyl cation formed on deamination of labelled cyclohexylamine has been investigated[66]. In the presence of the ClO_4^-, $H_2PO_4^-$, and CH_3COO^- anions, the degrees of isomerisation of this cation were 3.7 ± 0.3%, 5.0 ± 0.5%, and 3.7 ± 1.4% respectively. The absence of an appreciable influence of the change in the nucleophilic properties of the anions on the degree of isomerisation of the cation shows that the transition state is formed in all cases with participation of the molecules of the same substance derived from the solvent. This substance can apparently be only water. A change in the reaction temperature from 20° to 90 °C also does not affect the degree of isomerisation of the [1-^{14}C]cyclohexyl cation.

It is known that the reaction of aminomethylcycloalkanes with nitrous acid leads to cycloalkanols as a result of the rearrangement of cycloalkylmethyl cations to cycloalkyl cations. Thus, according to the data of Smith et al.[67], the reaction of aminomethylcyclopentane with nitrous acid leads to the formation, together with unsaturated hydrocarbons, of a mixture of alcohols whose main component is cyclohexanol:

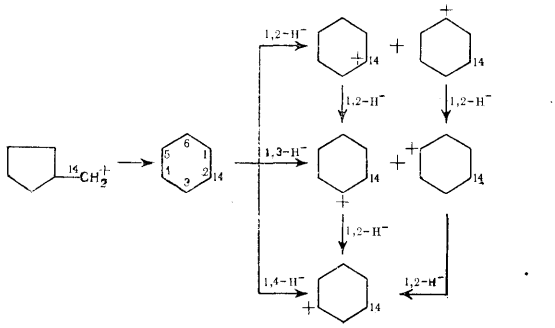


The question whether the cyclohexyl cation isomerises as a result of hydride shifts in the given reaction is of natural interest. In this connection a study was made of the reaction of aminomethylcyclopentane with nitrous acid using the ^{14}C isotope.[68] The reaction of aminomethyl[^{14}C]cyclopentane with nitrous acid was performed in an aqueous solution of sodium dihydrogen phosphate at 90 °C, as in the study of Smith et al.[67] The resulting mixture of alcohols was oxidised in order to isolate [^{14}C]cyclohexanone, which was subjected to degradation in accordance with the following scheme:



It follows from the radioactivities obtained that cyclohexanol contains ^{14}C not only in the 2-position but also in all the remaining positions, which indicates the isomerisation of the cyclohexyl cation. The cyclohexyl cation can isomerise as a result of hydride shifts from the 2,6-positions (the H$^-$1,2-shift), the 3,5-positions (the H$^-$1,3-shift), and the 4-position (the H$^-$1,4-shift) or as a result of consecutive shifts in accordance with Scheme 10:

Scheme 10



The distribution of the label among all the positions of the six-membered ring can be caused, generally speaking, both by independent H$^-$1,2-, 1,3-, and 1,4-shifts and by a combination of consecutive H$^-$1,2-shifts (and also H$^-$1,3–1,2-shifts). Shatkina et al.[68] left this question open believing that the isomerisation proceeds via independent H$^-$1,2-, 1,3-, and 1,4-shifts.

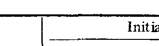
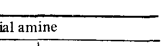
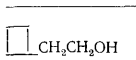
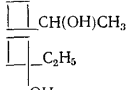
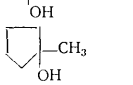
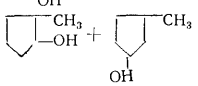
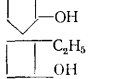
The difference between the relative radioactivities of cyclohexanone and pentamethylenediamine is 4.5%; according to Scheme 10, it corresponds to half the H$^-$1,2-shifts, whereas

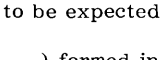
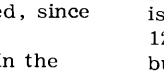
¶The low degree of rearrangement of the cyclohexyl cation may be explained by the fact that it reacts very rapidly with the solvent to form cyclohexanol. The fact that the reaction of *cis*-[2-D]cyclohexylammonium perchlorate with nitrous acid leads to the formation of at least 94% of *cis*-[2-D]cyclohexanol has been explained analogously[60].

the cyclohexyl cation isomerises to the extent of 9% as a result of H^-1,2-shifts. The radioactivity of methylamine (1.2%) is caused by half the H^-1,3-shifts, so that the cyclohexyl cation isomerises to the extent of 2.4% as a result of H^-1,3-shifts. The degree of isomerisation due to the H^-1,4-shifts is equal to the difference between the relative radioactivities of trimethylenediamine and half the sum of the percentage isomerisations due to the H^-1,2- and 1,3-shifts; this difference is 1.2%. Thus the [2-^{14}C]cyclohexyl cation formed as an intermediate in the reaction of aminomethyl[^{14}C]cyclopentane with nitrous acid isomerises to the extent of 12.6 ± 1.0% due to the hydride shifts.

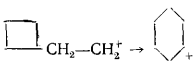
Interesting results were obtained in a study of the deamination of 1-cyclobutyl- and 2-cyclobutyl-ethylamines[69]†. The deamination was carried out in an aqueous solution of sodium dihydrogen phosphate at 90 °C; the results of the analysis of the reaction products are presented in Table 4.

Table 4. Deamination of 1-cyclobutyl- and 2-cyclobutyl-ethylamines.

Reaction products	Initial amine	
		
	37.4	4.4
	4.2	53.4
	17.4	6.9
	18.7	23.5
	14.3	7.6
	0.3	—
	17.4	6.9

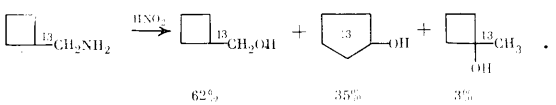
Inspection of the data in Table 4 shows that the deamination of 1-cyclobutyl- and 2-cyclobutyl-ethylamines entails the formation of a large amount of rearranged products. The set of alcohols isolated from the products of the first and second reactions is the same, but the degrees of rearrangement of the intermediate carbonium ions in the reactions investigated are different. The rearrangement accompanied by the expansion of the ring contributes 31–33% in both reactions. Apart from the skeletal rearrangement, the carbonium ions undergo a rearrangement as a result of the hydride ion shift. In the deamination of 2-cyclobutylethylamine the degree of rearrangement as a result of the migration of hydride ions, leading to products without ring expansion, is greater (39%) than in the case of 1-cyclobutylethylamine (20%). Evidently this was to be expected, since the primary carbonium ion () formed in the former case should rearrange to a much greater extent (to tertiary and secondary carbonium ions) than the more stable secondary carbonium ion () formed in the latter case.

The formation of large amounts of 1-, 2-, and 3-methylcyclopentanols in both reactions indicates a considerable tendency towards ring expansion in the intermediate cyclic carbonium ions. Ring expansion by two carbon atoms, leading to a cyclohexanol, takes place to a slight extent (0.3%) and only in the case of 2-cyclobutylethylamine. The absence of cyclohexanol from the deamination products of 1-cyclobutylethylamine indicates a one-stage rearrangement of the carbonium ion:



In the study of the deamination of aminomethylcyclobutane, we employed the ^{13}C DMNR method[71]. Dem'yanov and co-workers[74] showed that the deamination of aminomethylcyclobutane is accompanied by ring expansion and leads to the formation of cyclopentanol and the normal reaction products—cyclobutylmethanol; the yields and ratios of the products were not determined.

The earlier study of the deamination of aminomethyl[^{14}C]-cyclopentane and the demonstration of the rearrangement of the intermediate carbonium ion[68] made it of interest to study the deamination of aminomethyl[^{13}C]cyclobutane in order to observe the isomerisation of the carbonium ion leading to ring expansion. The deamination was carried out in an aqueous solution of sodium dihydrogen phosphate at 90 °C. The composition of the reaction products was determined by GLC and the distribution of the ^{13}C in the reaction products was found by the ^{13}C DNMR method[73]; the results of the analysis of the reaction products are presented below:



Inspection of the above data shows that the deamination of aminomethyl[^{13}C]cyclobutane results in the formation of a considerable amount of rearranged products. The contribution of the rearrangement accompanied by ring expansion is 35%. The formation of 1-methylcyclobutanol shows that, apart from the skeletal rearrangement, the carbonium ion isomerises due to the migration of the hydride ion, which leads to the formation of a tertiary cation.

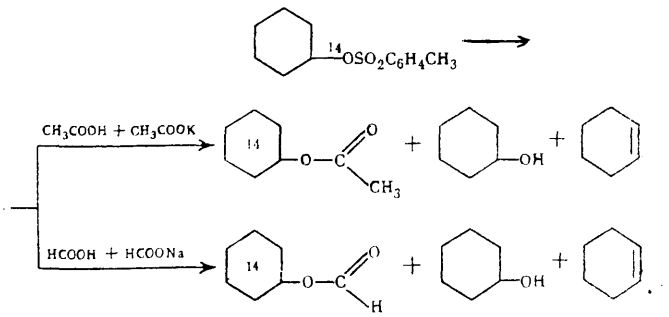
The distribution of the ^{13}C label in the cyclopentanol molecule was found from the ^{13}C DNMR spectrum. It was established that cyclopentanol contains ^{13}C not only in the 2-position but also in all the positions, which indicates the isomerisation of the intermediate carbonium ion owing to the migration of the hydride ion in the ring. In carrying out a comparison with data[68] for the isomerisation of the carbonium ion formed on deamination of aminomethyl[^{14}C]cyclopentane, one should note an appreciably greater degree of isomerisation due to hydride shifts (45% compared with 12.5%) of the carbonium ion formed from aminomethylcyclobutane and its smaller capacity for ring expansion (35% compared with 75%).

The stereochemistry of the Dem'yanov rearrangement and the influence of conformational factors on the latter have been studied in a number of investigations[75–77].

† The formation of rearranged products in the deamination of [1-^{14}C]-2-cyclopropylethylamine has been demonstrated[70].

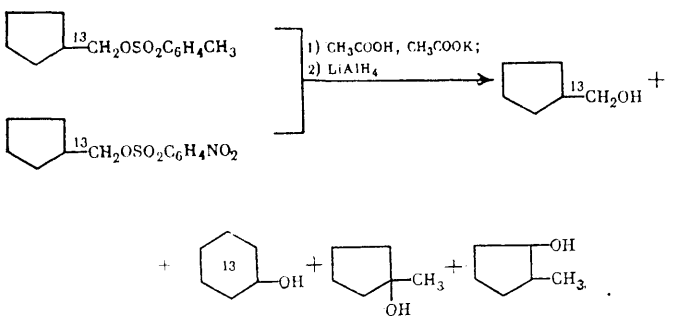
VII. THE ISOMERISATION OF CARBONIUM IONS IN SOLVOLYTIC REACTIONS

The isomerisation of the [1-^{14}C]cyclohexyl cation in acetolysis and formolysis has been studied[78]:



The solvolysis of [1-^{14}C]cyclohexyl toluene-*p*-sulphate was carried out by heating the latter with glacial acetic acid and potassium acetate at 50° and 100 °C or with anhydrous formic acid and sodium formate at 50 °C for 16 h. The cyclohexyl cation isomerises as a result of hydride shifts to the extent of 7% in acetolysis and 60% in formolysis. Analogous results were obtained in the study of the influence of the water content in the medium on the types of hydride shifts in the reaction of [2,6-D_2]cyclohexyl toluene-*p*-sulphonate.[79]

The acetolysis of cyclopentyl[^{13}C]methyl toluene-*p*-sulphonate and *p*-nitrobenzenesulphonate has also been studied[80]:



Analysis of the distribution of the label in the reaction products showed that the isomerisation due to hydride shifts takes place to the extent of 25% in the case of the toluene-*p*-sulphonate and 24% in the case of the *p*-nitrobenzenesulphonate.

The isomerisation of the cations formed as intermediates in the solvolysis of cyclopentylmethyl and cyclohexyl arenesulphonates labelled with ^{13}C or ^{14}C is significantly influenced by the ionising capacity of the medium and temperature; the influence of the leaving group is weak[81].

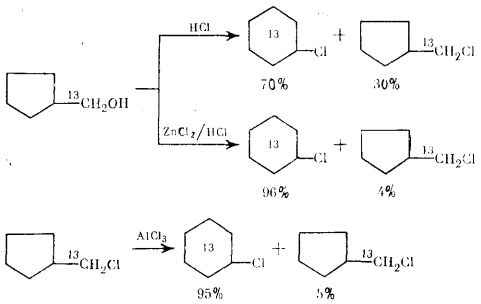
The following mixtures of products are formed in the acetolysis of cyclobutyl[^{13}C]methyl toluene-*p*-sulphonate and cyclobutyl[^{13}C]methyl *p*-nitrobenzenesulphonate:[82]

The distribution of ^{13}C in the cyclopentyl acetate molecule was determined by the ^{13}C DNMR method under the conditions of total uncoupling of the hydrogen nuclei[72]. The significant influence of the nature of the departing group on the rearrangement accompanied by ring expansion and conversely the absence of its influence on the isomerisation in the cyclopentane ring as a result of hydride shifts are noteworthy.

An analogous behaviour has been observed in the acetolysis of the corresponding 2-cyclobutylethyl arenesulphonates[83], as can be seen from the data in Table 5.

The hydride shifts were also investigated in the reactions of cyclic alcohols with the Lucas reagent ($ZnCl_2$/HCl).[84-88] Scheme 11 presents some of the reactions investigated, including the reaction with aluminium chloride[87]:

Scheme 11



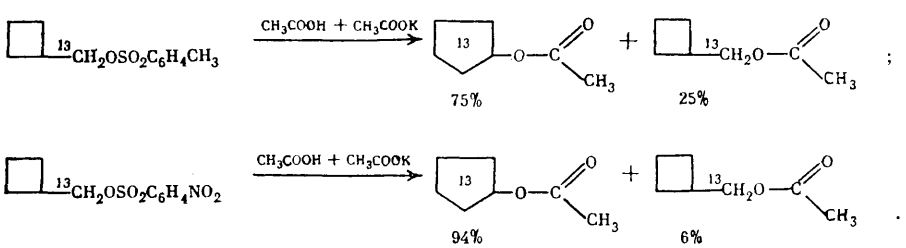
(3) (4) (5)

Table 5. The products of the acetolysis (rel.%) of 2-cyclobutylethyl toluene-*p*-sulphonate and *p*-nitrobenzenesulphonate.

Initial compound			 cis-	trans-		Ring expansion, %
	23.0	22.0	20.0	33.0	2.0	77
	5.0	37.0	20.0	34.0	4.0	95

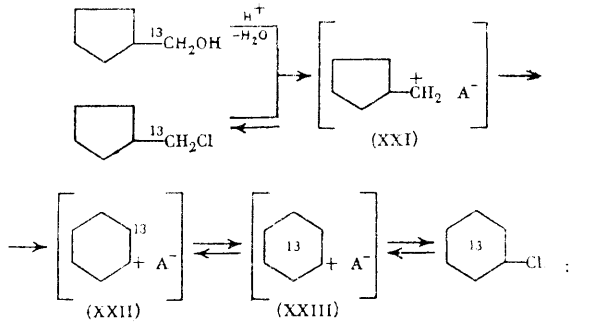
Note. Ns = *p*-nitrobenzenesulphonyl (Ed.of Translation).

The cyclohexyl chloride formed contains the label in all the positions in the cyclohexane ring and not only in the 2-position, as would have been the case in the absence of isomerisation. The virtually uniform distribution of the label in



the ring shows that the cyclohexyl cation undergoes the maximum possible isomerisation. One can imagine the following probable mechanism of the reactions: in the first stage the ion pair (XXI) is formed rapidly (as a result of the protonation of the carbinol with subsequent elimination of water or via the ionisation of cyclopentylmethyl chloride by the Lewis acids) and is in its turn irreversibly# converted into the ion pair (XXII) (Scheme 12):

Scheme 12



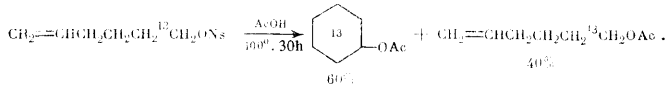
(XXI) (XXII) (XXIII)

$A^- = AlCl_4^-$, $ZnCl_3^-$, HCl_2^- .

The cyclohexyl cation stabilised by the complex anion is fairly stable and isomerises as a result of hydride shifts. Ion pairs of type (XXII) are formed and subsequently give rise to the reaction products.

The isomerisation of the cyclohexyl cation on heating cyclohexanol with boric acid has been investigated. The expansion of the cyclopentane ring to the cyclohexane ring has been discovered in the demercuration of cyclopentylmethylmercury acetate[90].

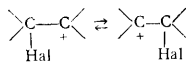
The acetolysis of [1-^{13}C]-5-hexenyl and cyclopentyl[^{13}C]methyl p-nitrobenzenesulphonates has also been investigated[91]. It has been found that the degree of cyclisation reaches 60% in the acetolysis of [1-^{13}C]-5-hexenyl *p*-nitrobenzenesulphonate after 30 h at 100 °C; the [^{13}C]cyclohexyl acetate formed has been fully isomerised, which has resulted in a uniform distribution of the label in the ring:



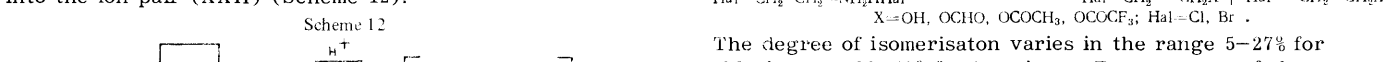
Analogous data have been obtained in the study of the acetolysis of cyclopentyl[^{13}C]methyl *p*-nitrobenzenesulphonate[80] under the same conditions in the absence of potassium acetate. A uniform distribution of the label was also obtained in the main reaction product, namely cyclohexyl acetate, which indicates the 100% isomerisation of the intermediate cation as a result of the migration of hydride ions. The equivalent results of these reactions suggest the formation of the same intermediate cation responsible for the isomerisation.

VIII. REARRANGEMENTS WITH THE 1,2-MIGRATION OF THE HALOGEN ATOM

Numerous rearrangements of carbonium ions due to the 1,2-migration of the halogen have been discovered in the study of a number of deamination and solvolytic reactions:



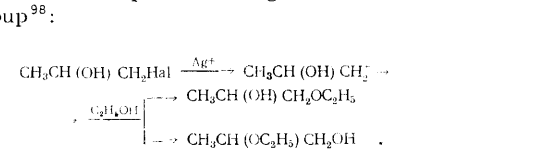
The simplest model reactions, namely the deamination of β-halogenoethylamines, have been studied using the ^{14}C label[92-96]:



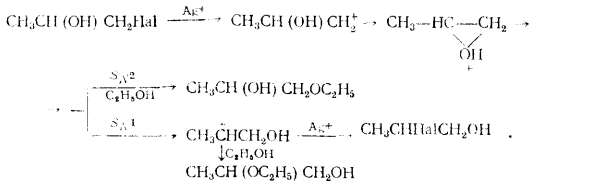
X = OH, OCHO, $OCOCH_3$, $OCOCF_3$; Hal = Cl, Br .

The degree of isomerisaton varies in the range 5–27% for chlorine and 30–50% for bromine. For a survey of the rearrangements and deamination reactions, see Reutov and Gudkova[97].

The alcoholysis of 1-halogeno-2-propanols and 2-halogeno-1-propanols in the presence of silver nitrate apparently proceeds with the nucleophilic 1,2-migration of the hydroxy-group[98]:



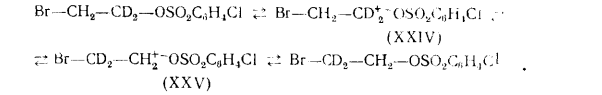
The authors quote the following hypothetical reaction mechanism:



In the solvolysis of the simplest model compounds, the degree of 1,2-migration of the halogen is as a rule higher than in the deamination reaction. Thus the degree of 1,2-migration of bromine reaches 50% in the course of the trifluoroacetolysis of [1-^{14}C]-2-bromoethyl arenesulphonates (Ar = Ph, *p*-ClC_6H_4, *p*-$CH_3C_6H_4$, or β-$C_{10}H_7$).[99] The acetolysis of 2-bromoethyl *p*-nitrobenzenesulphonate is accompanied by 40.8% 1,2-migration of the halogen[100]. As a rule, with the increase of the ionising power of the acid and with decrease of its nucleophilic properties, the degree of migration of the halogen increases[101,102]. Thus the degree of migration increases from 0 to ~4% for chlorine and from 33 to 56% for bromine in the solvolysis of [1-^{14}C]-2-halogenoethyl *p*-nitrobenzenesulphonates and *p*-bromobenzenesulphonates on passing from CH_3COOH to HCOOH and then to CF_3COOH.

In the acetolysis of halogenoethyl sulphonates in aprotic solvents, the degree of isomerisation increases with increasing polarity of the solvent. Thus the acetolysis of [1-^{14}C]-2-bromoethyl arenesulphonates in benzene is not accompanied by isomerisation at all, while in nitrobenzene the extent of the 1,2-migration of the halogen atom is 49%.

It is of interest to note that the isomerisation of the initial sulphonate, which had not reacted, was observed in the acetolysis of the [2,2-D_2]-2-bromoethyl *p*-chlorobenzenesulphonate. This isomerisation apparently takes place in the ion pairs (XXIV) and (XXV) with their reconversion into the covalent substrate:



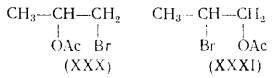
(XXIV) (XXV)

#The reversibility of this stage has been demonstrated by special experiments.

IX. THE ISOMERISATION OF ACYLOXYBROMOPROPANES

In the study of the products of the solvolysis of 1(2)-halogeno-2(1)-propyl tosylates $CH_3CH(OTs)CH_2Cl$ (XXVI), $CH_3CH(OTs)CH_2Br$ (XXVII), $CH_3CHClCH_2OTs$ (XXVIII), and $CH_3CHBrCH_2OTs$ (XXIX) in acetic acid, it was observed that the reaction products consist in each case of two halogenoalkyl acetates—unisomerised and isomerised as a result of the 1,2-migration of the halogen.

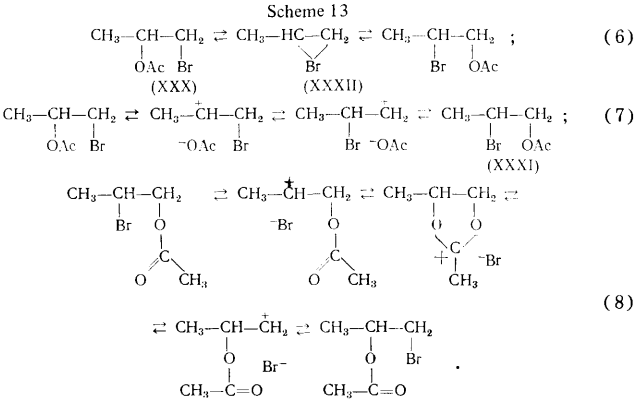
When these reactions are studied in the presence of sodium acetate, the picture becomes more complex[102]. For example, in the solvolysis of compounds (XXVII) and (XXIX), the products of secondary processes (1,2-dibromo- and 1,2-diacetoxypropanes) appear in addition to $CH_3CH(OAc)CH_2Br$ (XXX) and $CH_3CHBrCH_2OAc$ (XXXI), but the ratio of compounds (XXX) and (XXXI) remains the same as in the absence of added sodium acetate (70 : 30). These results led to the hypothesis that the acetoxybromopropanes formed undergo a reversible isomerisation owing to the 1,2-migration of bromine already in the acetolysis of the initial bromotosylates:



(XXX) (XXXI)

Indeed it has been shown[101] that, when pure compounds (XXX) and (XXXI) are heated in glacial acetic acid (for 30 h at 100 °C), the same equilibrium mixture, containing 70% of 1-bromo-2-propyl acetate and 30% of 2-bromo-1-propyl acetate, is formed. Three possible reaction mechanisms [(6), (7), and (8) in Scheme 13] were examined:

Scheme 13

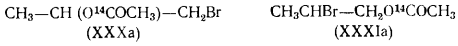


(6)

(7)

(8)

In order to discover which is the true mechanism of the isomerisation, the tracer atom method was employed[102]. The isomeric acetoxybromopropanes (XXXa) and (XXXIa) labelled with ^{14}C in the acetoxy-group were synthesised:



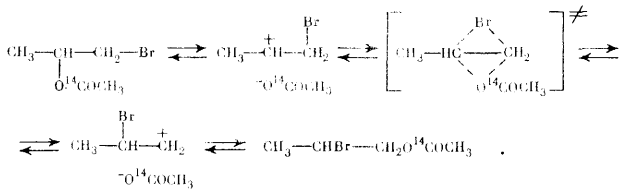
(XXXa) (XXXIa)

Each radioactive isomer was heated in glacial acetic acid for 30 h at 100 °C, i.e. until the attainment of equilibrium between the isomeric acetoxybromopropanes, after which the loss of radioactivity was compared with the degree of isomerisation. In both cases the isomerisation terminated with partial retention of the radioactive label in acetoxybromopropanes [16% for compound (XXXa) and 10% for compound (XXXIa)].

If the acetoxonium mechanism (7) operated, the complete retention of the radioactivity would have been observed, and in addition 1,2-diacetoxypropanes should have appeared in the reaction mixtures. The result of the isomerisation of the labelled compounds combined with the complete absence of 1,2-diacetoxypropane makes it possible to exclude the acetoxonium mechanism from consideration. If the reactions of compound (XXXa) and (XXXIa) with acetic acid proceeded via the S_N2 mechanism, the products would have been non-radioactive and non-isomerised acetoxybromopropanes. If the reaction proceeded exclusively via the formation of carbonium ions, an equilibrium mixture of acetoxybromopropanes with complete loss of radioactivity would have been formed.

Some retention of radioactivity can apparently be explained by the fact that the isomerisation proceeds at least partly in the stage involving the formation of contact or solvate-separated ion pairs. The isomerisation proceeds in this case via a synchronous mechanism as a consequence of the simultaneous migration of the bromine atom and the labelled acetoxy-group (Scheme 14):

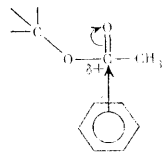
Scheme 14



The role of the main driving force leading to the formation of ion pairs in the given reaction is apparently assumed by the hydrogen bonds between the solvent molecules and the acetoxy-group in compounds (XXX) and (XXXI), although one cannot exclude *a priori* also the possibility that the dipole–dipole interaction between the molecules of acetic acid and the C–OAc bond plays a role.

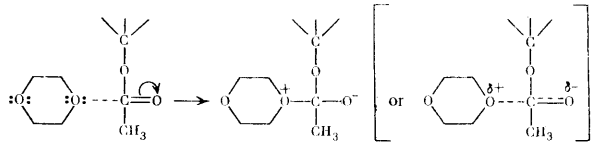
It is of interest that the isomerisation proceeds not only in acetic acid but also in benzene, toluene, and dioxane[101,102]. The isomerisation was carried out for 30 h at 100 °C and it was established that it proceeds only in those cases where the solvent molecules contain π or p electrons; the isomerisation does not occur in n-octane where such electrons are absent.

The isomerisation mechanism is apparently different from that in glacial acetic acid. Presumably in the case of aromatic solvents the main driving force of the reaction involves the interaction of the π-electron system of the benzene ring with the carboxyl carbon carrying a partial positive charge (the formation of a kind of π-complex):

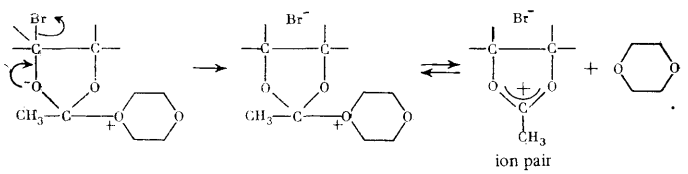


If this hypothesis is adopted, one may expect that this kind of interaction can also occur in solvents of the type of dioxane containing atoms with free p electrons and can be more intense than the interaction due to π-electron systems. The above interaction creates favourable conditions for the operation of the oxolonium mechanism (Scheme 15):

Scheme 15

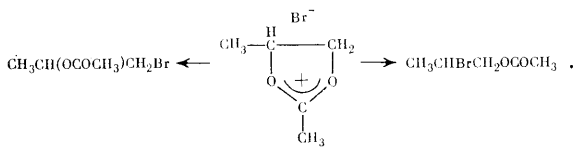


The carbonyl group activated in this way can probably play the role of an "internal" nucleophile in relation to the C—Br bond present in the molecule of the acetoxybromo-derivative:



ion pair

Next the ion pair can be stabilised by being converted into the isomeric acetoxybromopropanes:



The corresponding trifluoroacetoxybromopropanes do not isomerise. This is apparently due to the impossibility of the interaction of solvent molecules with the carboxyl carbon atom, examined above, owing to the steric hindrance generated by the three fluorine atoms. On the other hand, the corresponding trimethylacetoxybromopropanes (for which the steric hindrance is still greater) isomerise faster than acetoxybromopropanes and the reaction proceeds even in n-heptane. The stabilising influence of the t-butyl group on the acetoxonium cation formed apparently plays a decisive role in this case; the necessity for the activation of the carbonyl group by solvent molecules does not then arise.

* * *

We may note in conclusion that the development of the chemistry of alkyl radicals and alkyl cations can serve as a good illustration of the familiar postulate that science develops in jumps depending on the appearance of new research techniques. Thus qualitatively new results in the chemistry of carbonium ions are associated with the employment of superacid media, NMR, the tracer atom method, and in particular the ^{13}C double NMR. An equally great importance of the development and application of new research methods can be traced also in the chemistry of aromatic carbonium ions[103].

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Nesmeyanov Institute of Organoelemental Compounds,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 487-517 (1984) U.D.C. 541.515

The Structure and Stereochemistry of Paramagnetic Metal Complexes of *o*-Quinones

M.I. Kabachnik, N.N.Bubnov, S.P.Solodovnikov, and A.I.Prokof'ev

Data are presented on the EPR spectra of transition metal and Group IV metal complexes with *o*-semiquinone ligands. Analysis of the *g*-factors and the hyperfine coupling constants has been used to determine the structure of the complexes, the electronic configuration of the metal, and the ligand substitution processes.
The bibliography includes 56 references.

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I. INTRODUCTION

A new branch of the coordination chemistry of metals, associated with the extensive employment of *o*-quinone ligands, has arisen recently. As a result of the characteristic feature of the electronic structure of *o*-quinones, these ligands can function, depending on the conditions, as paramagnetic radical-anions, or diamagnetic catacholate dianions, or, in rare cases, as non-reduced *o*-quinone molecules. Thus, in contrast to the traditional task of coordination chemistry involving primarily the description of the electronic structure of the central metal ion, an additional task involving the determination of the degree of reduction of the ligand arises.

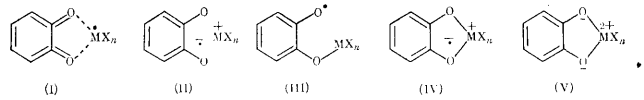
The interest in these systems at the present time is due to the exceptional wide variety of the electronic structures arising in such complexes. However, it was soon discovered that the complexes of *o*-quinones with certain transition metals are biochemically important. It was established that certain micro-organisms employ special substances—"siderophores"—as iron-binding agents.

One of these "siderophores", namely enterobactin, contains in its molecule three catechol groups joined via a macroring. The iron(III) complexes of enterobactin are exceptionally stable[1,2]. It is known that the conditions governing the growth of pathogenic bacteria are definitely related to the iron content in the human organism[3]. Thus the study of the formation and structure of variable-valence metal complexes of *o*-quinones has assumed practical importance.

Numerous studies of the structure of transition metal complexes of *o*-quinones by X-ray diffraction have been analysed in a review[4]. According to the latter[4], the length of the carbonyl bond C—O in the *o*-quinone is a characteristic quantity and makes it possible to estimate the degree of reduction of the ligand. The greatest number of stability constants of the complexes have been determined for the iron(III) ion. It was found that the iron(III) complex of enterobactin has the highest stability constant[5]. It was shown that the synthetic analogues of enterobactin and also of *o*-quinone, having a simple structure, form with Fe^{3+} complexes having high stability constants[5]. The chemical characteristics of transition metal complexes of *o*-quinones include their ability to undergo multistage oxidation and reduction with retention of their structure[4]. It can be assumed that donor—acceptor interactions constitute the basis of the reactions of these complexes with N_2, CO, and O_2. It has been found that the vanadium complexes of catechol actively fix molecular nitrogen under certain conditions[6]. The vanadium complexes also proved capable of reversible combination with O_2, NO, and CO.[7]

The formal examination of the electronic structure of metal complexes of *o*-quinones is usually carried out within the framework of the oxidation-reduction triad of the *o*-quinone. Taking into account the coordination, it is possible to postulate different structures of the complex of *o*-quinone with the organometallic fragment $\dot{M}X_n$ having an odd number of electrons. We shall consider paramagnetic complexes of precisely this type.

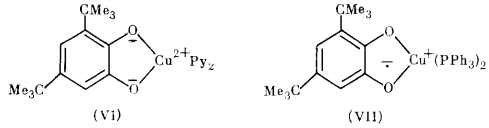
In principle, the *o*-quinone ligands can give rise to the following types of complexes:



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

The formation of a particular structure depends on the nature of M and X and on the number *n*. Structure (I) corresponds to the coordination of the neutral *o*-quinone via the unshared electron pairs of the oxygen atoms. Structures (II)—(IV) correspond to the coordination of the semi-reduced form of the quinone—the semiquinone radical-anion—and differ in the distribution of the unpaired electron between the metal and the ligand. Structure (V) reflects the coordination of the fully reduced quinone—the catecholate dianion.

The change in the degree of oxidation of the copper atom and of the degree of reduction of the ligand in the following complexes can serve as a clear example of the transformation of the structures[8,9]:



(VI) (VII)

The energy differences between structures (VI) and (VII) are small and the replacement of pyridine by triphenylphosphine leads to a sharp alteration of the electronic structure of the complex. In certain cases the possibility of equilibrium between forms (VI) and (VII) has been postulated,

as, for example, in the case of the bipyridyl adduct of the cobalt complex of 3,5-di-t-butyl-*o*-benzoquinone.[10] However, such hypotheses must be accompanied by an indication of the character of the skeletal changes in the complexes without which no transitions between the "electronic isomers" are of course possible. A convenient method for the investigation of the above transitions involves the photochemical synthesis of the complexes of *o*-quinones with radical organometallic fragments. In contrast to other methods[11–14], it makes it possible to determine not only the final reaction products but also the unstable intermediate complexes.

The coordination chemistry of Group IV elements has developed to a much lesser extent than that of transition metals. The employment of semiquinone paramagnetic ligands leads to new possibilities for the study of the stereochemistry of the coordination compounds of silicon and tin. Electron paramagnetic resonance (EPR) and electronic absorption spectroscopy have been used as the main procedures for the investigation of the electronic structure of the *o*-quinone complexes.

The aim of the present review was to examine the characteristics of the structures of the complexes and the wide variety of the electronic configurations of the metal and the ligands and to demonstrate the possibilities of the EPR method from the standpoint of the solution of various stereochemical problems.

II. THE ELECTRONIC STRUCTURE OF PARAMAGNETIC MANGANESE, RHENIUM, IRON, MOLYBDENUM, TUNGSTEN, AND CHROMIUM COMPLEXES OF *o*-QUINONES

1. The EPR and Electronic Absorption Spectra of the Complexes of *o*-Quinones with Manganese and Rhenium Penta- and Tetra-carbonyls

It is known that the photolysis of manganese and rhenium decarbonyls leads to the formation of the corresponding radicals[13]:

$$(CO)_5M—M(CO)_5 \xrightarrow{h\nu} 2\dot{M}(CO)_5,$$

where M = Mn or Re. The interaction of these radicals with *o*-quinones leads to the formation of complexes having different structures depending on the temperature.

When manganese pentacarbonyl was allowed to react with *o*-quinones, it was possible to detect primary radicals which had not been found in previous studies[16–19], to determine their stabilities, and to measure the rate constants for their reactions[22]. The photolysis of $M_2(CO)_{10}$ in the presence of 3,6-di-t-butyl-*o*-benzoquinone and pentane at −80 °C leads to the appearance of a radical whose EPR spectrum corresponds to the interaction of the electron with the ^{55}Mn ($I = 5/2$) nucleus and with the two non-equivalent protons of the catechol ligand (Fig.1).

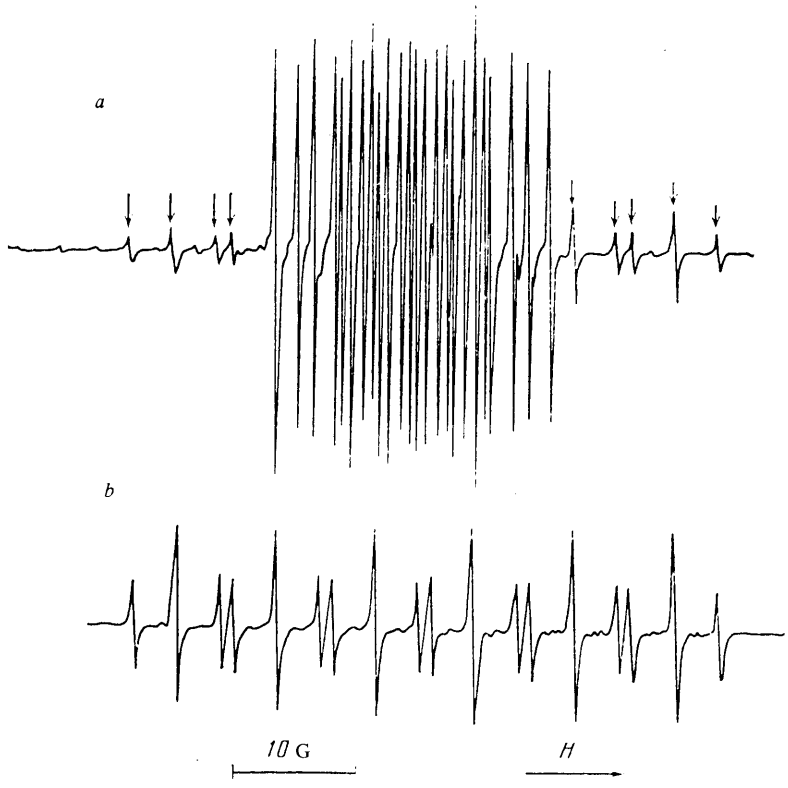
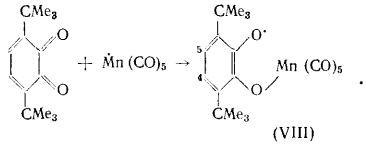


Figure 1. EPR spectra of the radicals (VIII) (*a*) and (IX) (*b*) in pentane at −80 °C (*a*) and 20 °C (*b*); the arrows indicate the lines of the radical (IX).[22]

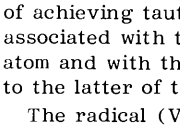
On the basis of the characteristics of the distribution of the unpaired electron density in the catechol ligand, a structure with the unpaired electron localised at the oxygen atom was attributed to the radical (VIII):



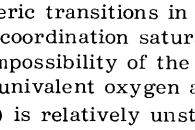
(VIII)

The larger hyperfine coupling contant (HFC) (5 G) is attributed to the ring proton in the 4-position relative to the univalent oxygen atom of the catechol ligand and the smaller constant (1.7 G) is attributed to the proton in the 5-position. In the temperature range from −100° to 20 °C, the alternation of the hyperfine structure (HFS) line widths is not manifested in the EPR spectra of the complex (VIII), which permits the conclusion that the $-M(CO)_5$ fragment does not migrate between the oxygen atoms of the catechol ligand in the radical (VIII) on the EPR time scale. The difficulty of achieving tautomeric transitions in this case is probably associated with the coordination saturation of the manganese atom and with the impossibility of the additional coordination to the latter of the univalent oxygen atom.

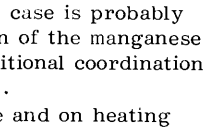
The radical (VIII) is relatively unstable and on heating above −80 °C is converted (in the absence of ultraviolet radiation) into the radical (IX), characterised by appreciable hyperfine coupling with the ^{55}Mn nucleus and with the two equivalent protons of the catechol ligand (Fig.1 and Table 1). Table 1 presents the spectroscopic characteristics of species having the following structures:



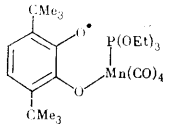
(IX)



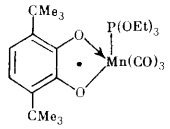
(X)



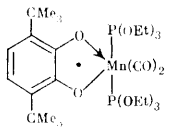
(XI)



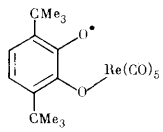
(XII)



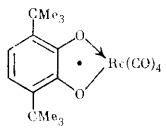
(XIII)



(XIV)

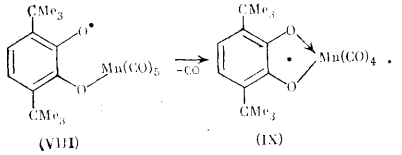


(XV)



(XVI)

Because of the low stability of the radical (VIII), the latter was not detected in previous studies[16–19]. There is controversy concerning the structures of the radicals (IX), namely whether they contain the $Mn(CO)_5$ or $Mn(CO)_4$ fragments. It has been suggested[16,17] that the fragment $Mn(CO)_4$ is present in radicals of type (IX). The data obtained by Tumanskii et al.[22] constitute important evidence in support of this hypothesis and the radical (IX) is probably formed on elimination of one CO group from the primary radical (VIII):



(VIII) (IX)

Table 1. The spectroscopic parameters (G) of the primary and secondary radicals formed on interaction of *o*-quinones with manganese and rhenium pentacarbonyls.[22,23]

Radical	$a_{H(4)}$	$a_{H(5)}$	a_{Mn}	a_P
(VIII)	5.0	1.7	3.0	—
(IX)	3.4	3.4	7.7	—
(X)	—	—	2.8	—
(XI)	—	—	8.7	—
(XII)	5.1	1.7	2.2	6.0
(XIII)	3.15	3.15	10.1	43.0
(XIV)	2.7	2.7	16.1	54.0
(XV)	—	—	6.6	—
(XVI)	3.8	3.8	29.0	—

Note: a_{Cl} = 0.47 G [the average of the constants for the hyperfine coupling of the unpaired electron with the $^{35}Cl(^{37}Cl)$nuclei] was obtained for the radical (XI); the constants for the hyperfine coupling of the unpaired electron with the ^{185}Re and ^{187}Re nuclei are quoted instead of a_{Mn} for the radicals (XV) and (XVI).

To confirm the transformation of the radical (VIII) into the radical (IX), a study was made of the kinetics of the destruction of the radicals (VIII) and of the accumulation of the radicals (IX), the analysis of which indicates the unimolecular character of the conversion of (VIII) into (IX) and the extremely similar rate constants for the destruction of the radicals (VIII) (3.0×10^{-3} s^{-1}) and for the accumulation of the radicals (IX) (3.3×10^{-3} s^{-1}) at −30 °C show that the radical (VIII) is almost entirely converted into the radical-(IX). The general expression for the rate constant for the unimolecular conversion of the radical (VIII) into the radical (IX) is[22]

$$k(s^{-1}) = 2 \cdot 10^{15} \exp[-(17300 \pm 1000)/RT]$$

and $k(-20\ °C) = 0.017\ s^{-1}$.

The stability of the primary manganese-containing radicals investigated depends significantly on the structure of the *o*-quinone employed. In the case of *o*-chloranil, the primary radicals (X) (see Table 1), which differ from the secondary radicals (XI) by the constants for the hyperfine coupling with the ^{55}Mn and ^{35}Cl, ^{37}Cl nuclei, proved to be much less stable than the corresponding complexes with the 3,6-di-t-butyl-1,2-dihydroxybenzene ligands. The rate of destruction of the radicals (X) proved to be appreciably higher than the rate of accumulation of the radicals (XI), which shows that, apart from the elimination of the CO group, the primary radicals derived from o-chloranil participate also in other destruction processes. However, the activation energies for the destruction of the radicals (X) and the accumulation of the radicals (XI) proved to be approximately identical. The overall expression for the rate constant for

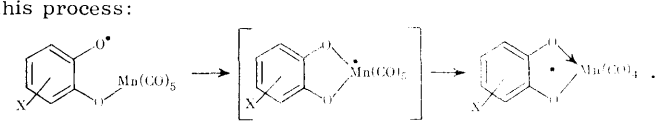
the transformaton of the primary radical (X) into the secondary radical (XI), determined from the curve for the accumulation of the secondary radical (XI), is

$$k(s^{-1}) = 5 \cdot 10^{8} \exp[-(7600 \pm 1000)/RT]$$

Triethyl phosphite (TEP) exerts a significant influence on the stability of the primary radicals. The photolysis of $M_2(CO)_{10}$ in the presence of 3,6-di-t-butyl-*o*-benzoquinone with added TEP leads to the appearance of a primary radical to which the structure (XII) was attributed (Table 1), with an asymmetric distribution of the unpaired electron density in the catechol ligand (this is indicated by the difference between the HFC constants for the ring protons) and with additional hyperfine coupling with the ^{31}P nucleus. The rate of conversion ($k = 0.0013\ s^{-1}$) of the radical (XII) into the secondary radical (XIII), characterised by the equivalent HFC constants for the ring protons and the much higher HFC constant due to the coupling with the ^{31}P nucleus, is appreciably lower than the rate of conversion of the radical (VIII) into the radical (IX) at −20 °C presented above[23].

After prolonged illumination of the reaction mixture in an excess of TEP, yet another CO group is substituted by a TEP molecule in the coordination sphere of manganese, and the radical (XIV), whose spectroscopic characteristics are listed in Table 1, is generated[23].

The large difference between the destruction constants of the primary radicals as a function of the structure of the ligands at the manganese atoms shows that the rate-limiting stage of the process is apparently intramolecular attack on the central manganese atom by the univalent oxygen atom of the catechol ligand. The electron-accepting properties of the ligand and the electron-donating properties of the manganese-containing fragment play an important role in this process:



The primary rhenium complexes (XV) and the secondary rhenium complexes (XVI), formed in the photochemical reacton of 3,6-di-t-butyl-*o*-benzoquinone with $Re_2(CO)_{10}$, have a much greater line width in the EPR spectra, in contrast to the analogous manganese-containing complexes, which leads in some cases to the blurring of the proton hyperfine structure. In the transition from (XV) to (XVI) a sharp increase of the constants for the hyperfine coupling with the ^{185}Re, ^{187}Re nuclei is observed (see Table 1).[23] It follows from Table 1 that the substitution of the CO group by a TEP molecule leads to an appreciable shift of the unpaired electron density from the *o*-quinone ligand to the manganese, rhenium, and phosphorus atoms.

Analysis of the EPR spectrum of the radical (VIII) demonstrates unambiguously the asymmetric addition of the *o*-quinone ligand to $\dot{M}n(CO)_5$. However, it is difficult to estimate the polarity of the bond between the ligand and $\dot{M}n(CO)_5$ from the difference $a_{H(4)} - a_{H(5)}$. To solve this problem, a study was made[20] of the electronic absorption spectra of the test complexes. Fig.2 illustrates the electronic absorption spectra of the manganese complexes (VIII), (IX), (XIII), and (XIV) in pentane. On heating from −100° to 20 °C, it is possible to observe a successive decrease of the intensity of the bands of (VIII) and an increase of the band of (IX). An analogous behaviour has been observed also in the transformation of the rhenium complexes. Table 2 presents the spectroscopic data for the complexes investigated. In the spectra of the complexes (VIII) and (XV), the primary complexes of manganese and rhenium, there are two absorption bands in the visible region: near 600 nm and a more intense band in the range 400–500 nm. The spectra of the complexes (IX) and (XVI), the secondary complexes of manganese and rhenium, contain one band in the visible region. A band in the ultraviolet region with $\lambda_{max} \approx$ 300 nm has been observed in the spectrum of a rhenium complex of type (XVI) with the 3,5-di-t-butyl-1,2-dihydroxybenzene ligand. The extinction coefficients of such complexes, determined by Gerber and Wan[21], amount to $\sim 10^3$ litre mole^{-1} cm^{-1}.

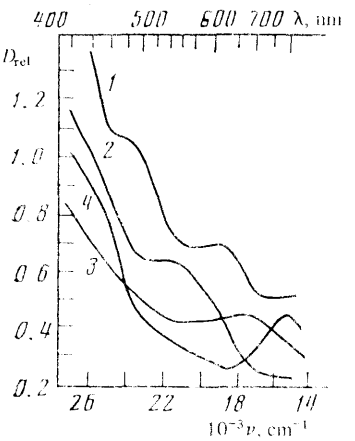


Figure 2. Electronic absorption spectra of manganese complexes in pentane: *1*) (VIII) at −100 °C; *2*) (IX) at 20 °C; *3*) (XIII) at −150 °C; *4*) (XIV) at 20 °C.

Table 2. The frequencies of the π–π* transitions in the electronic absorption spectra of the *o*-semiquinone complexes of manganese and rhenium carbonyls[20].

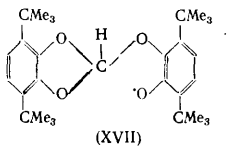
Complex	Solvent	ν, cm^{-1}
$Q^{\cdot-}Mn^{I}(CO)_5$	Toluene	16500; 20800
$Q^{\cdot-}Mn^{I}(CO)_5$	Pentane	16500; 21000
$Q^{\cdot-}Re^{I}(CO)_5$	Toluene	16000; 20800
$Q^{\cdot-}Mn^{I}(CO)_4$	Toluene	17000
$Q^{\cdot-}Mn^{I}(CO)_4$	Pentane	19200
$Q^{\cdot-}Re^{I}(CO)_4$	Toluene	20000
$Q^{\cdot-}Re^{I}(CO)_4$	Pentane	20800
$Q^{\cdot-}Mn^{I}(CO)_3P(OEt)_3$	Pentane	13000
$Q^{\cdot-}Mn^{I}(CO)_2[P(OEt)_3]_2$	Pentane	12500
$Q^{\cdot-}Re^{I}(CO)P(OEt)_3$	Pentane	17200
$Q^{\cdot-}Re^{I}(CO)_2[P(OEt)_3]_2$	Pentane	15000
$Q^{\cdot-}Mn^{I}(CO)_3NBu_3$	Pentane	14500
$Q^{\cdot-}Mn^{I}(CO)_3(CH_3)_2CO$	Acetone	18800(20 °C), 21200(−50 °C)
$Cl_3Q^{\cdot-}Mn^{I}(CO)_4$	Hexane	16000

Notation: Q = 

Successive substitution of two CO groups in the complex (IX) by two TEP molecules[22,23] leads to a strong bathochromic shift of the band at 540 nm (Fig.2). When the reaction is carried out at temperatures between −20° and −15 °C, a band, corresponding to the complex (XIV), appears at 670 nm. On further heating, the 670 nm band disappears.

and a new band with λ_{max} = 800 nm appears; when the reaction is carried out at room temperature, this band appears at once. After the measurement of the spectra of (IX) and (XIV), part of the soluton was transferred to a tube for the investigation of the EPR spectra. The signal splittings due to the interaction with the nuclei of hydrogen, manganese, and phosphorus atoms, observed in the EPR spectra[22,23], confirm the assignment of the bands in the electronic spectra to species having the corresponding structure. Analogous shifts of the long-wavelength absorption band on substitution of the CO groups by TEP take place in the corresponding rhenium complexes (XVI). A bathochromic shift is observed also in the spectra of the complex (VIII) in the presence of tributylamine, which indicates the substitution of the CO group by an amine molecule.

The similarity of the spectroscopic characteristics of the manganese and rhenium complexes (VIII) and (XV) and the complexes (IX) and (XVI) is associated with the similarity of their structures and the fact that the chromophore responsible for their absorption in the visible region is an *o*-semiquinone ligand. Although the electronic absorption spectra of certain *o*-semiquinone radical-anions had been obtained earlier[24-26], the influence of coordination on the positions of the absorption bands had not been investigated. In order to consider the spectra of the manganese and rhenium complexes, a study was made of the influence of the coordination of the Na^+ cation and the *o*-semiquinone ligand on the spectrum of the corresponding sodium *o*-semiquinolate (O^-Na^+) in tetrahydrofuran (THF) and the electronic absorption spectrum of the radical (XVII), in which the catechol ligands are bound covalently to the central carbon atom, was measured:



(XVII)

Fig. 3 illustrates the spectra of Q^-Na^+ at 70° and −70 °C. At −70 °C the 770 nm band shows a shoulder at 660 nm, which disappears on heating and reappears on cooling. According to Prokof'ev[27], the fraction of contact ion pairs in THF increases with decrease of temperature (ΔH = 1.7 ± 0.2 kcal mol^{-1}) and for this reason we assigned the shoulder at 660 nm to two contact ion pairs. Thus the coordination of the ions in Q^-Na^+ leads to an appreciable hypsochromic shift and an increased time of contact between this complex and a sodium mirror results in the decolorisation of the solution associated with the formation of a diamagnetic dianion. The spectrum of the dianion has a single absorption maximum at 305 nm. For comparison, we shall indicate the positions of the absorption band maxima of the corresponding catechol derivative (270 nm) and the orthocarbonic ester of catechol, which is a precursor of the radical (XVII) (270 nm). When air is admitted into the cuvette containing the dianion, the characteristic blue colour of the radical-anion reappears and its spectrum is measured.

The electronic spectrum of the radical (XVII), obtained by oxidising the corresponding phenol with lead dioxide, contains a band with λ_{max} = 400 nm, on which there are two shoulders, at 380 and 420 nm.[20] It follows from these data that, in the presence of a covalent bond at the second oxygen atom, a larger hypsochromic shift of the absorption bands is observed in the spectrum of the radical than that of the bands due to the *o*-semiquinone radical-anion. Comparison of the spectra of the complexes (VIII) and (IX), on the one hand, and those of (XV) and (XVI), on the other, with the spectra of Q^-Na^+ (Fig. 3) demonstrates a great similarity both in the positions of the bands and their intensities. Such similarity indicates a high polarity of the metal–oxygen bond and that the ligand is present in the radical-anionic form[28].

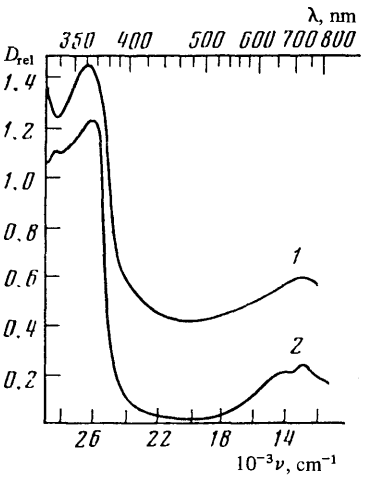


Figure 3. Electronic spectra of the radical-anion $Q^-(Na^+)$ in THF at 70 °C (curve *1*) and −70 °C (curve *2*).[20]

The involvement of the second oxygen atom in the bond with the metal in the complexes (VIII) and (XVI) leads to an appreciable hypsochromic shift of the bands in the absorption spectrum, which may be associated with a definite contribution of a covalent chelate structure, arising as a result of the effective exchange interaction between the d_{xz} and d_{yz} orbitals of the metal and the π electrons of the ligand[20].

2. The EPR Spectra of the *o*-Quinone Complexes of Iron, Molybdenum, and Tungsten Metallocenes

The substitution of the CO groups in iron, molybdenum, and tungsten carbonyls by the cyclopentadienyl ligand leads to an alteration of the even number of *d* electrons of the metal to an odd number, which results in the possibility of the formation of dinuclear complexes. It is believed that the cyclpentadienyl ligand in the dimeric complex $[Mo(CO)_3 . \pi\text{-}C_5H_5]_2$ has a negative charge, is a donor of three electron pairs, and occupies three coordination sites, the molybdenum atom having a formal +1 oxidation state and a coordination number of 7.[29] The photolysis of such dimers leads to the appearance of the corresponding metal-centered radicals, which react with *o*-quinones to form paramagnetic complexes[30].

The EPR spectra of the paramagnetic complexes arising on photolysis of $Fe_2(\pi\text{-}C_5H_5)_2(CO)_4$, $Mo_2(\pi\text{-}C_5H_5)_2(CO)_6$, and $W_2(\pi\text{-}C_5H_5)_2(CO)_6$ in the presence of 3,6-di-t-butyl-*o*-benzoquinone, 3,5-di-t-butyl-*o*-benzoquinone, and *o*-chloranil (3,6-Q, 3,5-Q, and Cl_4Q respectively) have been investigated[43]. The primary paramagnetic products detected in the temperature range −100° to −60 °C in a 2 : 1 pentane–toluene mixture have spectra whose common feature is an asymmetric distribution of spin density in the *o*-quinone ligand [$a_{H(4)} \neq a_{H(5)}$], which reflects the non-equivalent involvement of the oxygen atoms in the formation of a bond

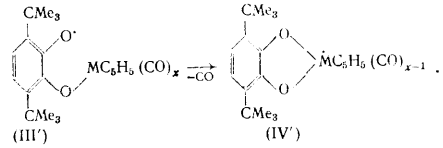
between the ligand and the metal. The HFC constants and the g-factors are listed in Table 3.

Table 3. Parameters of the EPR spectra of the adducts of $FeC_5H_5(CO)_3$ and $WC_5H_5(CO)_3$ with o-quinones[43].

Complex	$a_{H(4)}$, G	$a_{H(5)}$, G	a_M, G	$\tilde{g}$	g_1	g_2	g_3
(III′) 3,6-QFeC$_5$H$_5$(CO)$_2$	4.6	1.5	—	2.001	—	—	—
(III′) 3,5-QFeC$_5$H$_5$(CO)$_2$	—	2.8	—	2.000	—	—	—
(IV′) 3,6-QFeC$_5$H$_5$CO	—	—	—	2.048	2.104	2.033	2.006
(IV′) 3,5-QFeC$_5$H$_5$CO	—	—	—	2.046	—	—	—
(III′) 3,6-QMoC$_5$H$_5$(CO)$_3$	5.3	0.9	—	2.003	—	—	—
(III′) 3,5-QMoC$_5$H$_5$(CO)$_3$	—	2.3	—	2.002	—	—	—
(IV′) 3,6-QMoC$_5$H$_5$(CO)$_2$	1.0	1.0	15.6	1.990	—	—	—
(XIX) (3,6-Q)$_2$MoC$_5$H$_5$	—	—	37.3	1.868	1.989	1.971	1.952
(XIX) (3,5-Q)$_2$MoC$_5$H$_5$	—	—	36.4	1.968	1.990	1.972	1.949
(XIX) (Cl$_4$Q)$_2$MoC$_5$H$_5$	—	—	38.8	1.965	1.991	1.976	1.941
(XIX) 3,6-Q(Cl$_4$Q)MoC$_5$H$_5$	—	—	—	—	1.990	1.975	1.945
(III′) 3,6-QWC$_5$H$_5$(CO)$_3$	6.9	0.8	—	1.999	—	—	—
(III′) 3,5-QWC$_5$H$_5$(CO)$_3$	—	3.8	—	2.001	—	—	—
(XIX) (3,6-Q)$_2$WC$_5$X$_5$	—	—	72.5	1.902	1.960	1.912	1.842
(XIX) 3,6-Q(Cl$_4$Q)WC$_5$H$_5$	—	—	—	—	1.960	1.923	1.824

Note: 3,6-Q = 3,6-di-t-butyl-1,2-dihydroxybenzene ligand; 3,5-Q = 3,5-di-t-butyl-1,2-dihydroxybenzene ligand; Cl$_4$Q = o-chloranil ligand. Compexes of type (III′) all have the structure of phenoxy-radicals, while complexes of type (IV′) have chelate structures with the predominant localisation of the unpaired electron at the metal atom (see text).

In contrast to the complexes of manganese and rhenium pentacarbonyls, the ligand-centered free radicals considered in this section are converted into new metal-centered free radicals (Table 3):



In the case of molybdenum and tungsten, the metal-centered free radicals undergo further changes associated with the substitution of the CO groups by the o-quinone.[43]

The EPR spectra of the liquid and solid solutions of the metal-centered free radicals are presented in Figs.4–6. The change in the g-factor in solution relative to its value for the free electron, the strong anisotropy of the g-factor and the absence of an appreciable hyperfine coupling with the hydrogen atoms of the ligands in solution show that the unpaired electron occupies the 3d(Fe), 4d(Mo), and 5d(W) orbitals of the corresponding metal atoms. Analysis of the EPR spectra of the solid solutions shows that the paramagnetic species are characterised by an overall spin $S = 1/2$ in all cases.

In the radicals of the type $\dot{M}(C_5H_5)(CO)_x$ the iron, molybdenum, and tungsten atoms should have the $3d^7$, $4d^5$, and $5d^5$ configurations respectively. The number of d electrons of the metal atom in the complex depends on the degree of

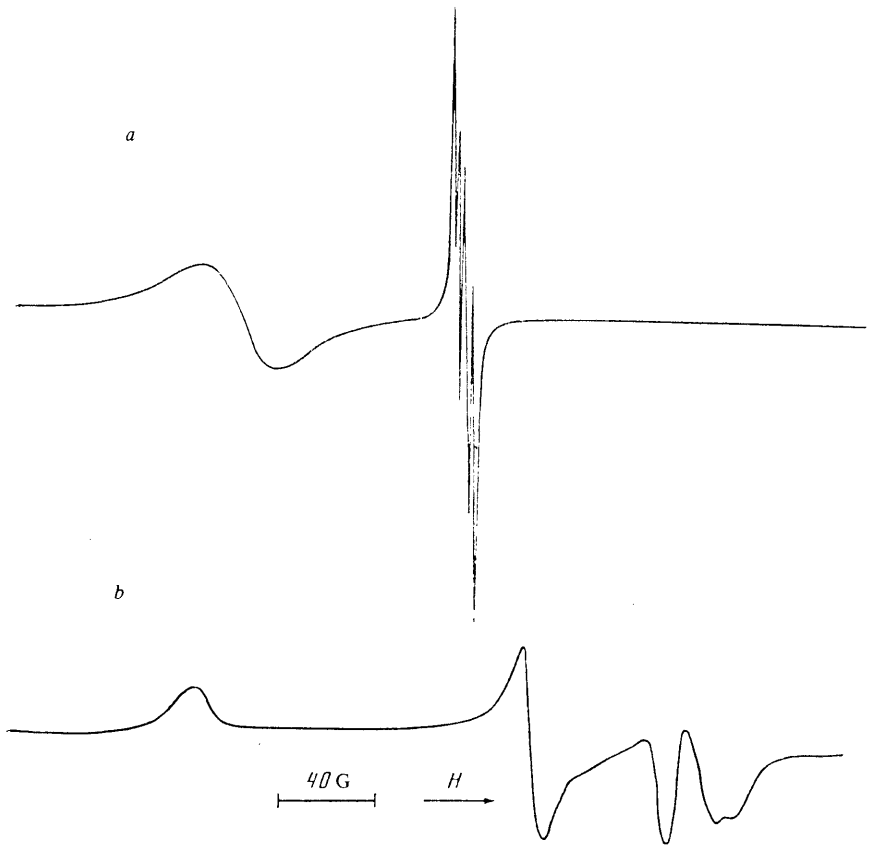


Figure 4. EPR spectra of 3,6-QFeC$_6$H$_5$CO: a) solution, −75 °C; b) solid solution, 155 °C.[43]

its oxidation by the *o*-quinone ligands. Depending on the degree of reduction of the *o*-semiquinone ligand (from semiquinone to the catecholate), the metal atom loses one or two electrons. When metal-centered free radicals are formed from $\dot{M}(C_5H_5)(CO)_x$ and *o*-quinones, a bond should be formed either by two electrons of the catecholate anion or by the unshared electron pairs of the oxygen atoms of the carbonyl groups in the non-reduced form of the quinone. The nature of the bond between the *o*-quinone ligands and metals has been investigated by X-ray diffraction[31,32].

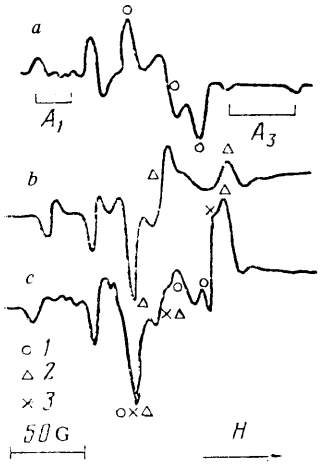
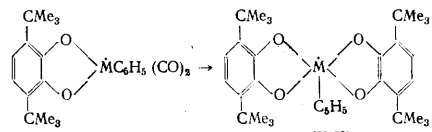


Figure 5. EPR spectra of solid solutions of molybdenum complexes: *a*) $(3,6\text{-Q})_2\dot{M}oC_5H_5$, −150 °C (*1*); *b*) $(Cl_4Q)_2.\dot{M}oC_5H_5$, −155 °C (*2*); *c*) mixture of $(3,6\text{-Q})_2\dot{M}oC_5H_5$ (*1*), $(Cl_4Q)_2MoC_5H_5$ (*2*), and $3,6\text{-QCl}_4\text{Q}\dot{M}oC_5H_5$ (*3*), −150 °C, 3,6-Q/Cl_4Q = 1; A_1 and A_3 are the components of the tensor of the hyperfine coupling with the ^{95}Mo(^{97}Mo) nuclei[43].

For the iron complexes, it is necessary to make a choice between the $3d^7$ and $3d^5$ electronic structures. For the $3d^7$ configuration, the non-reduced *o*-quinone is coordinated, while in the case of the $3d^5$ configuration the complex should have a catecholate linkage. According to Buchanan et al.[31], in the tris-*o*-quinone complexes of iron, all the ligands are reduced to the semiquinone state only. On the basis of these data, one can postulate that in the metal-centered complexes of 3,6-Q and 3,5-Q with $Fe(C_5H_5)(CO)_2$ the non-reduced form of the *o*-quinone is coordinated. It is of interest that the replacement of 3,6-Q and 3,5-Q by *o*-chloranil (Cl_4Q), which has more pronounced electron-accepting properties, leads solely to ligand-centered radicals characterised by a *g*-factor close to 2. Comparison of the spectra illustrated in Fig.6 with EPR spectra of arenecyclopentadienyliron,[33] in which the iron atom has the $3d^7a_{1g}^2e_{2g}^4.e^{*1}_{1g}$ configuration (d_{xz} and d_{yz} are the orbitals of the unpaired electron) demonstrates the similarity of the *g*-factors and of the degrees of their anisotropy. It may be that the presence of the cyclopentadienyl ligand in these two different complexes is responsible also for the analogous disposition of the *d* levels[33].

More complex reactions are observed for the molybdenum and tungsten complexes. The primary ligand-centered radicals are converted into metal-centered radicals of two types: the first has the structure (XVIII) and the second has the structure (XIX) (see Table 3):[43]



The radicals of type (XVIII) are unstable and are converted into the radicals (XIX) in the presence of an *o*-quinone. Complexes of type (XVIII) are characterised by $g < 2$, but the deviations from 2 are not as great as in complexes of type (XIX); the *g*-factor for the complex (XVIII) (M = Mo) is almost isotropic. The spectrum of this radical is characterised[43] by an HFC constant of 15.6 G corresponding to coupling with the ^{95}Mo(^{97}Mo)nuclei ($I = 5/2$) and with two protons of the catechol ligand. We may note the small (~1 G) splitting by the protons compared with the splitting of 3.5 G characteristic of the corresponding *o*-semiquinolates.

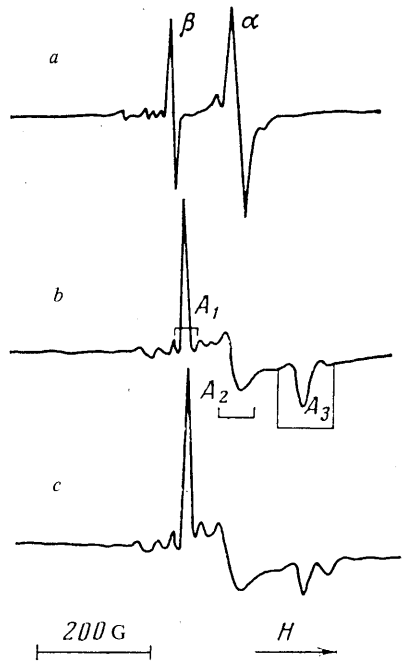


Figure 6. EPR spectra of tungsten complexes: *a*) $(3,6\text{-Q})_2.\dot{W}C_5H_5$ (α, the satellite lines due to ^{183}W are visible) at −20 °C (*1*) and $(3,6\text{-Q})_2\dot{M}oC_5H_5$ (β) present in solution as a consequence of a slight admixture of $Mo_2(C_5H_5)_2(CO)_6$ in the initial dimer $W_2(C_2H_5)_2(CO)_6$; *b*) $(3,6\text{-Q})_2\dot{W}C_5H_5$, −155 °C ($A_1$, A_2, and A_3 are the components of the tensor of the hyperfine coupling with the ^{183}W nuclei); *c*) mixture of $(3,6\text{-Q})_2WC_5H_5$ (*1*) and $3,6\text{-QCl}_4\text{Q}WC_5H_5$ (*2*), −155 °C.[43]

It is so far difficult to put forward a mechanism for the transfer of spin density from the metal atom and to estimate its value in the *o*-quinone ligand. One can only claim that in the secondary molybdenum complex there is one *o*-quinone ligand symmetrically attached to the molybdenum atom. The substitution of the remaining two CO groups in the radical (XVIII) (M = Mo) by the *o*-quinone ligand decreases the average *g*-factor and leads to the appearance of a considerable anisotropy of the latter (see Fig.5 and Table 3) and to an increase of the constant for hyperfine coupling with the ^{95}Mo(^{97}Mo)nuclei.[43]

The factors g_2 and g_3 proved to be sensitive to the structure of *o*-quinone following the replacement of 3,6-Q and 3,5-Q by Cl_4Q^-. The presence of two molecules of the *o*-quinone ligand in the complex (XIX) has been confirmed by the formation of mixed complexes. The interaction of $Mo(C_5H_5)(CO)_3$ with a mixture of 3,6-Q and *o*-chloranil produces, together with $(3,6\text{-Q})_2Mo(C_5H_5)$, also the complexes $(Cl_4Q)_2Mo(C_5H_5)$ and $(3,6\text{-Q})(Cl_4Q^-)Mo(C_5H_5)$.[43] The formation of $(3,6\text{-Q})(Cl_4Q)Mo(C_5H_5)$ was inferred from the appearance of a new line characterised by a value of g_3 different from that for the individual complexes of 3,6-Q and Cl_4Q. The relative intensities of the signals of the individual and mixed complexes depend on the ratio of the *o*-quinones 3,6-Q and Cl_4Q. The value of g_3 for the mixed complex is approximately equal to its average value for the individual complexes[43].

An analogous behaviour has been observed in the study of tungsten-containing complexes. The metal-centered radical (XVIII) is less stable and does not accumulate at high concentrations, being rapidly converted into the radical (XIX). The spectra of the tungsten complexes (XIX) exhibit larger shifts of the *g*-factor and a higher degree of anisotropy of the latter compared with the molybdenum complexes, possibly as a consequence of the larger spin-orbital coupling constant[34]. The interaction with a mixture of 3,6-Q and Cl_4Q results in the formation of mixed complexes characterised by smaller values of g_3 than for the 3,6-Q complex; the individual complex (XIX) with Cl_4Q is not formed. The parameters of the spin-Hamiltonian for the molybdenum complex (XIX) are close to the analogous parameters of the inorganic oxo-complexes described in the literature[35]. In the complexes $MoOX_4Y$ the molybdenum atom is located in the same plane as the ligands X_4; the complex has the C_{4v} symmetry, which is reflected by the axial symmetry of the *g*-factor, persisting even in mixed complexes of the type $MoOX_{4-i}Y_{i+1}$.[35] Presumably the absence of axial symmetry in the complexes investigated is associated, on the one hand, with the presence of the cyclopentadienyl ligand and, on the other hand, with the absence of the C_{4v} symmetry in the disposition of the oxygen atom relative to the $Mo-C_5H_5$ bond.

The electronic structure $4d^1$, with localisation of the unpaired electron in the d_{xy} orbital lying in the plane of the ligand X_4, is characteristic of the oxomolybdenum(V) complexes. The parameters of the spin-Hamiltonian of the oxo-complexes are extremely sensitive to the substitution of the ligand X_4.[35] In the oxo-complexes of *o*-quinones there is a catecholate linkage with the molybdenum(VI) atom[36]. All these factors suggest that the electronic configuration $4d^1$, with localisation of the unpaired electron in the d_{xy} orbital, is characteristic of the complex $Q_2MoC_2H_5$. An analogous hypothesis can apparently be put forward also for the tungsten complex in view of the similarity of the EPR spectra.

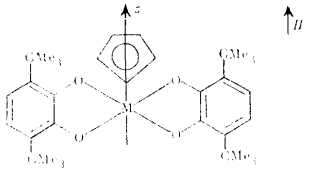
This hypothesis is confirmed by the analysis of the anisotropy of the *g*-factor and the anisotropic component of the HFC constant for the molybdenum and tungsten complexes. Having adopted the $4d^1$ state of the unpaired electron (the d_{xy} orbital) as the ground state and having neglected the delocalisation of the unpaired electron density over the ligand, we obtain the following expressions:

$$g_z = 2 - \frac{8\xi_M}{E_{d_{x^2-y^2}} - E_{d_{xy}}};\quad g_x = 2 - \frac{2\xi_M}{E_{d_{xz}} - E_{d_{xy}}};\quad g_y = 2 - \frac{2\xi_M}{E_{d_{yz}} - E_{d_{xy}}}.$$

Hence it follows that most probably $g_z = g_3$.

It follows from Figs.5 and 6 that there is no axial symmetry of the anisotropic hyperfine coupling either. The values $A_1 = 41$ G, $A_2 = 60$ G, and $A_3 = 112.5$ G for the tungsten complex (XIX) ($I^{183}W = 1/2$) can be determined from the EPR spectrum of a frozen solution, illustrated in Fig.6*b*. The value $\bar{A} = (A_1 + A_2 + A_3)/3 = 71.2$ G is close to $A_{iso} = 72.5$ G determined from the spectrum of the solution (Fig.6*a*). The values $A_1 = 66.0$ G and $A_3 = 65.0$ G for the complex $(3,6\text{-Q})_2MoC_5H_5$ can be determined from the spectrum; $A_2 = 113.0$ G has been calculated from the relation $A_{iso} = (A_1 + A_2 + A_3)/3$.

The dipole–dipole components of the HFC constant (A^P) can be determined from these data. For the molybdenum complex, we have $A_1^P = -2.0$ G, $A_2^P = 25.0$ G, and $A_3^P = 27.0$ G, while for the tungsten complexes the corresponding values are −31.5, −12.5, and 40.0 G. The identical signs of A_3^P and A_{iso}^P are consistent with the fact that the unpaired electron occupies the d_{xy} orbitals and the values of g_3 and A_3 correspond to the orientation of the *z* axis parallel to the external magnetic field[36].

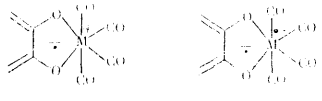


On the basis of the above considerations concerning the electronic structure of the molybdenum and tungsten complexes of type (XIX), one can postulate that complexes of type (XVIII) should also have the $4d^3$ and $5d^3$ configurations.

Transition metal complexes with *o*-quinone ligands can be obtained by the photochemical reaction of *o*-quinones with metal carbonyls. The photolysis of $Mo(CO)_6$ in the presence of 3,5-di-t-butyl-*o*-quinone, *o*-chloranil, and phenanthrenequinone yields complexes of different compositions[4,14]. The compositions were established by X-ray diffraction and were found to be represented by the formulae $\{MoO[O_2C_6H_2\cdot(t\text{-Bu})_2]_2\}_2$ for 3,5-di-t-butyl-*o*-quinone,[36] $Mo(O_2C_6Cl_4)_3]_2$ for *o*-chloranil,[37] and $(PhenQ)_2Mo_2O_5(PhenQ)_2$ for phenanthrenequinone.[38]

There is at present not only no clear-cut idea about the mechanism of these reactions and about the dependence of the final products on the nature of the *o*-quinone but even the source of the oxygen atoms of the oxomolybdenum group is not known exactly. Although $MoO[O_2C_6H_2(t\text{-Bu})_2]_2$ was synthesised in an N_2 atmosphere, the possible role of the presence of traces of oxygen in the formation of the main reaction product has been assumed[36]. The application of the EPR method to the study of the reaction mechanism did not yield an umambiguous answer to the question of the structure of the paramagnetic species detected and of their role in the formation of the final diamagnetic products[4,28].

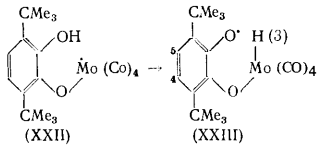
On the basis of the analysis of the EPR spectra of the semiquinone species arising in the photolysis of tungsten and molybdenum hexacarbonyls in the presence of phenanthrenequinone, formula (XX) was attributed to these species.



(XX) (XXI)

Here the metal is in the +1 oxidation state[28]. Since the unpaired electron of the ligand in compounds of type (XX) arises as a result of electron transfer from a metal atom having an odd number of electrons, in reality the metal atom should also carry an unpaired electron and the system as a whole should have a biradical character; formula (XXI) corresponds to this situation.

The reaction between $Mo(CO)_6$ and 3,6-di-t-butyl-*o*-quinone (3,6-Q) in pentane under vacuum conditions on irradiation with the light of a mercury lamp at room temperature is accompanied, as in the study of Weir and Wan[28], by the formation of the *o*-quinone radical-anions without any signs of hyperfine coupling with the molybdenum isotopes. Weir and Wan[28] present some arguments in support of the assignment of the measured spectra to a complex of type (XX) but, in view of the absence of hyperfine coupling with the magnetic molybdenum isotopes, this assignment cannot be regarded as unambiguous. When the above reaction is carried out at low temperatures, species whose EPR spectra are characterised by the following HFC constants are formed: $a_{H(3)}$ = 0.16 G, $a_{H(4)}$ = 3.8 G, $a_{H(5)}$ = 3.0 G, and a_{Mo} = 1.9 G.[54] The low constants for hyperfine coupling with one of the protons in the ^{95}Mo and ^{97}Mo isotopes enabled Sarbasov et al.[54] to propose the oxygen-centered structure (XXIII) for the species formed. The small difference between the constants for the hyperfine coupling with the protons in the fourth and fifth-positions of the aromatic ring shows that the bond between the central molybdenum atom and oxygen is polar under these conditions:

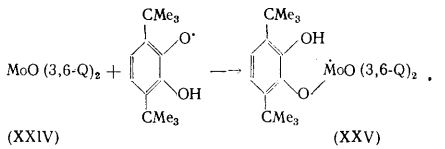


The formation of the radical (XXIII) should apparently be preceded by the formation of the metal-centered radical (XXII). The formation of these radicals is probably associated with the involvement of the semiquinone radical, functioning as a monodentate ligand. The participation of the semiquinone radical in the reaction is indicated by the increase of the concentration of the radicals (XXIII) when hydroquinone is added to the system.

Thus the reaction of the photoexcited quinone with hydrogen atom donors must be added to the primary photochemical step in the formation of the complexes, consisting in the elimination of the CO group from $Mo(CO)_6$.[28,29] After prolonged photolysis (~30 min) at a low temperature, a paramagnetic complex, in which the unpaired electron is localised at the molybdenum atom, accumulates gradually together with the unstable radical (XXIII).[54] When the reaction is carried out at room temperature, the radical (XXIII) is not formed at a concentration sufficiently high for measurement, but an increase of temperature does not affect the formation of the molybdenum-centered free radical. This radical is stable at room temperature *in vacuo* but disappears when oxygen is admitted into the tube.

The identification of the paramagnetic complex described as a molybdenum-centered free radical is based on the following spectroscopic data: the appreciable difference of the *g*-factor from 2, the appreciable anisotropy of the *g*-factor, and the large constants for splitting by the Mo nuclei[54].

According to the results of chemical analysis[36], one can postulate the formation of mainly the diamagnetic product $MoO[O_2C_6H_2(t\text{-}Bu)_2]_2$. The presence of the M=O bond in the photolysis product follows from the formation of the paramagnetic complex when the reaction mixture is treated with HCl,[54] because the *g*-factor and the HFC constant for the complex formed are fully consistent with the known values for $MoOCl_5$.[35] The similarity of the spectral parameters of the radicals listed in Table 4 is striking. On this basis, one can suggest that these spectra correspond to radicals arising via the reaction[54]



The interaction of (XXIV) and (XXV) with HCl leads to the formation of $MoOCl_5$.

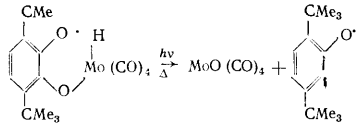
It follows from Table 4 that the parameters of the EPR spectra depend on the solvent and on the structure of the *o*-quinone. The influence of THF is evidently associated with complex formation.

Table 4. The *g*-factors and the constants for the hyperfine coupling with the molybdenum nucleus in the hydroxy-molybdenum complexes of *o*-quinones[54].

Complex	a_{Mo}, G	$\bar{g}$	g_1	g_2	g_3
(XXV) in THF*	46.5	1.953	1.985	1.945	1.945
(XXV) in pentane	51.9	1.939	1.961	1.940	1.917
$MoOCl_5$ in THF	51.9	1.946	1.968	1.942	1.942

*Axial symmetry.

It follows from the analysis of the X-ray diffraction data that the *o*-quinone ligand in $(MoOQ_2)_2$ [36] accepts two electrons from the metal atom and is a catecholate dianion. The source of the oxygen atoms in the oxomolybdenum group remains unelucidated. The formation of the M–O bond *in vacuo* suggests that the source of the oxygen atoms is some kind of complex of the *o*-quinone whose cleavage gives rise to the M=O bond, for example:



The photolysis of $Mo(CO)_6$ in toluene in the presence of di-t-butyl peroxide also leads to the appearance of a signal with a slightly anisotropic *g*-factor (g = 1.931), tentatively identified as $t\text{-}BuOMo(CO)_4$.

3. The Electronic Structure of the Tris-3,6-di-t-butyl-*o*-quinone Complexes of Chromium

Numerous studies have now been devoted to the tris-*o*-quinone complexes of chromium[4,39]. They are believed to be the closest analogues of the bacterial iron complex of the siderphore enterobactin[40]. There is so far no unanimous view concerning the electronic structure of these complexes. On the basis of the analysis of the X-ray diffraction data for the tris-3,5-di-t-butyl-*o*-quinone complex of chromium, Downs et al.[41] concluded that the Cr^{3+} ion is coordinated to three semiquinone ligands. After analysing the same data, Sofen et al.[39] concluded that the Cr^{3+} ion is coordinated to non-reduced *o*-quinone molecules. The difference between the studies of Downs et al.[41] and Sofen et al.[39] is associated with the fact that the former authors estimated the degree of reduction of the ligand from the length of the C–O bond,

while the latter estimated it from the length of the C–C bonds in the ring. According to polarographic data, the complexes should reversibly accept and give up six electrons[39,41]. The electronic absorption spectra of the tris-3,5-di-t-butyl-*o*-quinone complex of chromium and of its mono-, di-, and tri-anions in the visible region have been recorded[39].

The EPR spectra of the radical-cations and radical-anions exhibit a surprising similarity, which is manifested in the similarity of the constants for hyperfine coupling with the ^{53}Cr nuclei and of the *g*-factors.[55] The appreciable deviation of the *g*-factor from 2.0023 and the large splitting by ^{53}Cr (20–30 G) show that an appreciable fraction of the unpaired electron in the radical-cations and radical-anions is localised at the chromium atom[4,41]. It has been suggested that, on passing from the radical-cation to the radical-anion, the levels of the metal and ligands are inverted, so that in both cases the d_{z^2} orbital of the chromium atom accommodates the unpaired electron[4].

Until recently, there were no data on the distribution of the unpaired electron density among the *o*-quinone ligands, without which the description of the distribution of the spin density is incomplete. Such data have been obtained in a study[55] of the EPR spectra of the radical-cations and radical-anions of the tris-3,6-di-t-butyl-*o*-quinone complexes of chromium. The corresponding radical-cation and radical-anion were obtained by oxidising the tris-3,6-di-t-butyl-*o*-quinone complex of chromium with I_2 and by reducing it with the sodium and potassium salts of n-Bu_4NOH in solution in THF. The radical-cation is reformed on treating the radical-anion with I_2. The reversibility of the reduction has been established by the EPR method and electronic absorption spectroscopy. Figs.7 and 8 present the EPR spectra of the radical-cations and radical-anions of the complexes. The EPR spectrum of the radical-cation is characterised by the following parameters: $g = 1.9689$, $a_{Cr} = 25.5$ G, and $a_H = 0.85$ G.

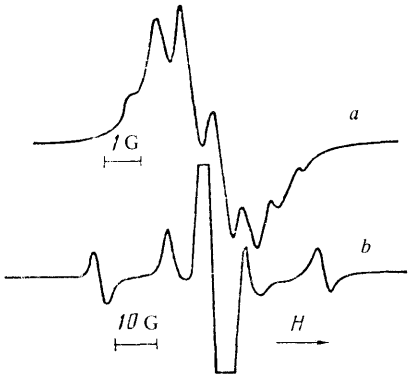


Figure 7. EPR spectrum of the radical-cation $Cr(3,6\text{-}Q)_3^+I^-$ in THF; spectrum *b* was recorded with tenfold amplification relative to spectrum *a*.[55]

For the semiquinone type of distribution of spin density in the ligand, there is a splitting of 0.85 G which corresponds to a spin density of 0.7 in the three *o*-quinone ligands, since the corresponding splitting in the radical-anion of 3,6-di-t-butyl-*o*-quinone is 3.6 G. This implies that the maximum spin density, amounting to 0.3, corresponds to the chromium atom, while in an individual ligand it amounts to 0.23.

The EPR spectrum of the radical-anion is characterised by the following parameters: $g = 1.9707$, $a_{Cr} = 22.7$ G, and $a_H = 0.85$ G.[55] The main difference between the spectrum of the radical-anion and that of the radical-cation consists in a decrease of the hyperfine coupling with ^{53}Cr and an appreciable increase of the line width. The best resolution is observed in the temperature range from 0° to −20 °C. At these temperatures, one of the wings of the envelope curve in Fig.8 shows clearly three HFS components. Presumably the number of lines is not less than seven, i.e. the unpaired electron density is delocalised over three ligands in the radical-anion, as in the radical-cation. It has been observed that the HFS pattern is independent of the nature of the cation (sodium or potassium).

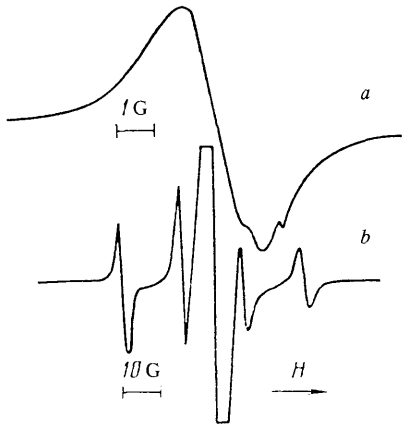
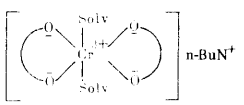


Figure 8. EPR spectrum of the radical-anion $Cr(3,6\text{-}Q)_3^-Na^+$ in THF; spectrum *b* was recorded with twentyfold amplification relative to spectrum *a*.[55]

Thus it follows from the data obtained that the distribution of spin density in the radical-anion is the same as in the radical-cation. Previously it had been assumed that in the paramagnetic chromium complexes the bulk of the unpaired electron density is located at the chromium atom[4]. We can now claim that the bulk of the spin density is in fact located in the ligands and not at the chromium atom.

The EPR spectra of the di-*o*-quinone complexes of chromium in the radical-cationic and radical-anionic forms have also been obtained[55]. These complexes are formed on prolonged treatment of the electrically neutral complex with oxidants and reductants and also as a result of the photochemical reactions of 3,6-di-t-butyl-*o*-quinone with $Cr(CO)_6$. In contrast to the tris-*o*-quinone complexes, the character of the distribution of spin density in the radical-cations and radical-anions of the di-*o*-quinone complexes of chromium is completely different. Five HFS components with a binomial distribution of intensities and the splittings $a_H = 0.85$ G and $a_{^{53}Cr} = 25.5$ G are clearly seen in the EPR spectrum of the radical-cation obtained by the prolonged treatment of $Cr(3,6\text{-}Q)_3$ with I_2. It follows from these data that the spin densities are 0.46 in the two ligands and 0.54 at the chromium atom[55].

After the reduction of $Cr(3,6\text{-}Q)_3$ with n-butyl alcohol, the EPR spectrum of the reaction mixture shows, apart from the signals due to the chromium atoms, $(3,6\text{-}Q)_3^{\bullet-}$, and $(3,6\text{-}Q)^{\bullet-}$, a narrow signal with chromium satellites (a_{Cr} = 16.0 G).[55] The narrow signal is apparently due to the radical-anion $Cr(3,6\text{-}Q)_2^{\bullet-}$, which is formed after the elimination of $(3,6\text{-}Q)^{\bullet-}$ from the initial radical-anion. The absence of hyperfine coupling with the ligand protons indicates the localisation of the unpaired electron at the chromium atom, which led to the assignment of the biscatecholate structure (XXVI) to these species:



(XXVI)

Analysis of the parameters a_{Cr} for the test complexes shows that they are influenced by the spin densities both at the chromium atom and at the oxygen atoms. The radical-cations described above are obtained on photolysis of 3,6-Q and $Cr(CO)_6$. In this case they are formed either under the influence of traces of O_2 or on irradiation[55].

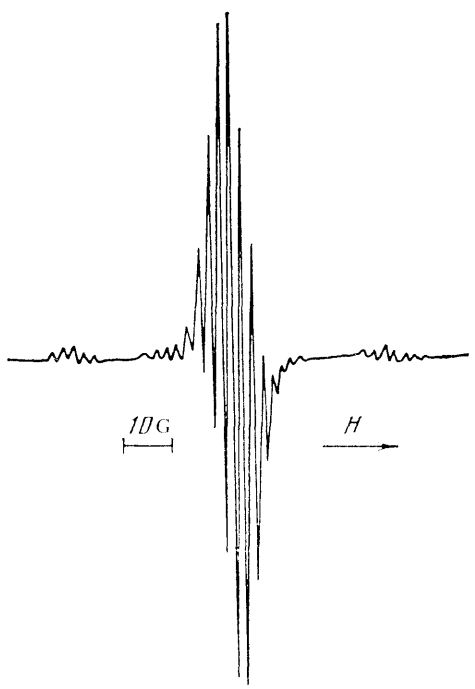


Figure 9. EPR spectrum of the radical cation $Cr(CF_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}\overset{O}{\overset{\|}{C}}\text{–}CF_2CF_3)_2^{+\bullet}$.[42]

In addition to the tris-3,6-Q complexes of chromium, the di-*o*-quinone complexes of chromium are also formed in coordinating solvents (ether, THF, and alcohol). It is noteworthy that, after the photolysis of a solution of 3,5-Q and $Cr(CO)_6$ in toluene, the EPR spectrum exhibits a HFS corresponding to the three protons of the three *o*-quinone ligands; the splittings are $a_H \cong 1.00$ G and a_{cr} = 26.9 G, while g = 1.9731.[55]

Fig.9 presents the EPR spectrum obtained on photolysis of $CF_3\text{–}\overset{O}{\overset{\|}{C}}\text{–}\overset{O}{\overset{\|}{C}}\text{–}CF_2\text{–}CF_3$ in an α-diketone in the presence of $Cr(CO)_6$. Analysis of the HFS shows that there are two α-diketone ligands in the radical-cation complex (a_F = 2.8 G, a_{cr} = 27 G, and g = 1.9658). The parameter a_F = 8.8 G has been obtained for the corresponding semidione complex of $Mn(CO)_4$, where the unpaired electron is localised in the ligand[42]. It follows from a comparison of these data that 0.6 of the unpaired electron density in the radical-cation complex of chromium corresponds to the two ligands and 0.4 corresponds to the chromium atom. Presumably two coordination sites in the two-ligand complexes are occupied either by CO groups or solvent molecules.

Whereas the distribution of the spin density of the unpaired electron can be inferred from EPR data, the distribution of the charge can be postulated solely on the basis of indirect data. For the purpose of further study of the electronic structure of the complexes, their electronic absorption spectra were obtained. Previously Solodovnikov et al.[20] investigated the influence of coordination on the positions of the absorption bands of the semiquinone chromophore in relation to the carbonylmanganese and carbonylrhenium complexes of 3,6-Q. Comparison of the spectrum of $Cr(3,6\text{-}Q)_3$ with that of $Cr(3,5\text{-}Q)_3$ [39] showed the complete identity of the positions and intensities of the absorption bands in the visible regions: in the ultraviolet region[55], a band was recorded at 290 nm (Fig.10). Comparison of the positions and intensities of the absorption bands in the $Cr(3,6\text{-}Q)_3$ spectrum with the positions and intensities of the absorption bands in the spectra of $(3,6\text{-}Q)^{\bullet-}Na^+$ and $(3,6\text{-}Q)^{\bullet-}\,Mn^+(CO)_4$ [20] as well as other manganese and rhenium complexes leads to the conclusion that the electronic configuration of the complex is much closer to that of $Cr^{3+}(3,6\text{-}Q)_3^{\bullet-}$ than to the configuration of the complex $Cr(3,6\text{-}Q)_3$.[55]

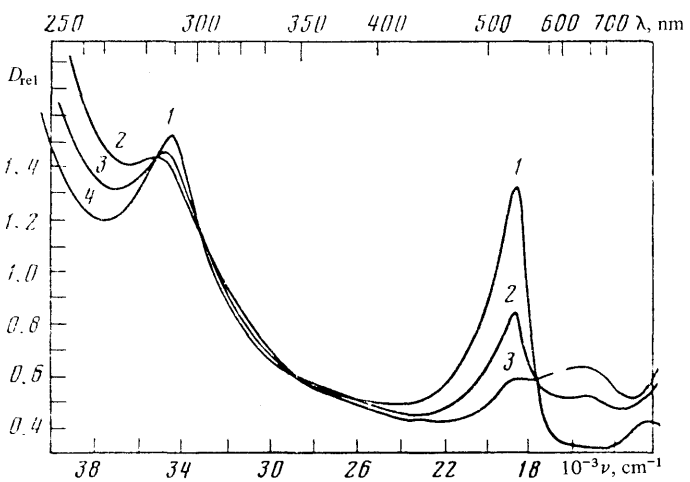


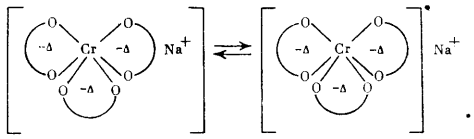
Figure 10. The changes in the electronic absorption spectra of $Cr(3,6\text{-}Q)_3$ during reduction by n-Bu_4NOH in THF: *1*) $Cr(3,6\text{-}Q)_3$; *2*) spectrum corresponding to the intermediate reduction stage; *3*) $Cr(3,6\text{-}Q)_3^{\bullet-}n\text{-}Bu_4N^+$.[55]

The reduction of the complexes *in vacuo* on a sodium mirror leads to a sharp decrease of the intensity of the 525 nm band and to the appearance of new absorption bands

at 520, 575, and 680 nm and a band with $\lambda_{max} > 800$ nm, which can probably be identified, on the basis of the study of Sofen et al.[39], as the 825 nm band. Measurement of the spectra in the course of the reduction of the complex revealed an isosbestic point; the spectrum *3* has been assigned to $Cr(3,6\text{-}Q)_3^{\bar{}}$.[55]

The large number of absorption bands in the spectrum of $Cr(3,6\text{-}Q)_3^{\bar{}}$ is striking. In view of this and also in view of the behaviour of the line width in the EPR spectrum of the complex $Cr(3,6\text{-}Q)_3^{\bar{}}Na^+$, the problem arises as to the form of the distribution of negative charge and spin density and of the influence of the cation on this distribution. In order to solve this problem, the complex was reduced by $n\text{-}Bu_4NOH$ (Fig. 10). The spectrum of $Cr(3,6\text{-}Q)_3^{\bar{}}n\text{-}Bu_4N^+$ differs from that of $Cr(3,6\text{-}Q)_3^{\bar{}}Na^+$ by the absence of the band at 575 nm.

The study of the influence of temperature on the spectrum of $Cr(3,6\text{-}Q)_3^{\bar{}}Na^+$ showed that the intensity of the 575 nm band diminishes appreciably when the temperature is reduced from 50° to −70 °C. This entails some increase of the intensity of the 680 nm band. Presumably the 575 nm absorption band is associated with the formation of a contact pair:



The temperature dependence of the width of the EPR line of the radical-anion may be partly associated both with the presence of this equilibrium and with the migration of Na^+ between the ligands in the contact and solvent-separated ion pairs. The use of $n\text{-}Bu_4N^+$ as the cation does not entail line narrowing. The subsequent reduction of $Cr(3,6\text{-}Q)_3^{\bar{}}Na^+$ on a sodium mirror leads to the disappearance of the 575 and 825 nm bands. The spectrum of $Cr(3,6\text{-}Q)_3^{2-}.2Na^+$ in the visible region consists of two bands at 516 and 720 nm. On reduction with atmospheric oxygen, the spectrum of the dianion gradually disappears and that of the radical-anion reappears; the radical-anion is stable in air for a long time.

The oxidation of the complex by oxidants such as I_2 and $AgBF_4$ is accompanied by a decrease of the intensity of the 525 nm band and the appearance of a new band at 365 nm in the electronic absorption spectra.

The experimental data presented yield a qualitative picture of the electronic structure of $Cr(3,6\text{-}Q)_3$ and its oxidised and reduced forms. We established that the degree of reduction of the ligand in $Cr(3,6\text{-}Q)_3$ is close to that in the semiquinone, while in the radical-cation and the radical-anion most of the spin density (0.7) is located in the ligands. On this basis, one can postulate that the number of electrons in the ligands of the radical-cation should be close to an odd number, for example 2.7; the number 1.7 no longer satisfies this condition. When the negative charge in the ligand is −2.7e, the charge on the chromium atom should be +3.7e. The number of electrons in the ligand of the radical-anion should be 4.7 and the charge on the cation should be +3.7e. Presumably in the electrically neutral complex the same charge of +3.7e on the chromium atom remains and the overall charge of the ligands is −3.7e. According to this picture, the charge on the chromium ion (+3.7e) in the complex does not change on oxidation and reduction.

According to the proposed charge distribution in the ion pairs involving the radical-cations and radical-anions, a completely different interaction between the counterions should be observed: in the former case there should be a weak interaction owing to the shielding of the positive charge on the chromium atom by the negatively charged ligands and in the latter case there should be a strong interaction due to the high negative charge on the ligands. The differences between the widths of the EPR lines of the radical-cations and radical-anions, caused by the difference in the dynamics of the redistribution of the spin and charge densities between the ligands and the complex, may be associated with this factor.

In conclusion it is useful to compare the spin density on the chromium atom, which amounts to 0.3, with the spin density in the ligand (0.23). The localisation of the unpaired electron either in the ligand (Mn, Re) [22,23] or at the central metal atom (W, Mo) [43] is characteristic of the majority of the transition metal complexes with semiquinone or catechol ligands investigated hitherto. The similarity of the spin densities on the chromium atom and in one of the ligands indicated above demonstrates the approximately equal involvement of their orbitals in the formation of a bond. Thus one may conclude that the Cr=O bond is highly covalent. It may be that the high degree of covalence of the M−O bond is the cause of the high complex forming capacity of enterobactin towards Fe^{3+} and Cr^{3+}.

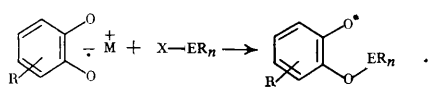
III. THE STEREOCHEMISTRY OF PARAMAGNETIC CHELATE COMPLEXES OF GROUP IV ELEMENTS WITH SEMIQUINONE LIGANDS

Within the framework of the electronic structures (I)–(V), the degree of reduction of the *o*-quinone ligand in the paramagnetic complexes of Group IV elements is −1. The main task of the study is to determine the coordination of the semiquinone ligand and the structure of the complex. Depending on the same variables (M, X, and *n*), not only are different types of coordination observed [structures (III) and (IV)] but also there is a significant variation in the geometrical disposition of the ligands X relative to the central atom M. Whereas the octahedral structure is characteristic of transition metal complexes of *o*-quinones, for the complexes of Group IV elements considerable variety of different types of environment of the central atom is observed. Analysis of the hyperfine coupling of the unpaired electron of the *o*-semiquinone ligand with the magnetic moments of the nuclei of the elements incorporated in the ligand X makes it possible to infer the geometrical disposition of these elements.

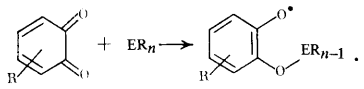
The different dispositions of the ligands relative to the plane (the nodal plane for the π orbitals of the unpaired electron localised in the *o*-semiquinone ligand) formed by the atom M and two oxygen atom is manifested by the equal values of the HFC constants. The non-equivalence of the oxygen atoms in the chelate coordination of the *o*-semiquinone ligand can arise in its turn in structures characterised by a trigonal-bipyramidal geometry of the disposition of the ligands X around the atoms M. This non-equivalence should be manifested by the inequality of the constants for the hyperfine coupling of the unpaired electron with different ring protons of the ligand [for example, $a_{H(4)} \neq a_{H(5)}$ in the case of the 3,6-di-t-butyl-1,2-dihydroxybenzene ligand].

Chelate *o*-semiquinone complexes of Group (IV) elements can be obtained from the following reactions.

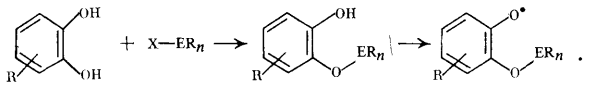
1. The interaction of alkali metal *o*-semiquinolates with organometallic halogeno-derivatives:



2. The interaction of *o*-quinones with organometallic compounds:

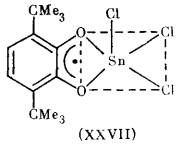


3. The interaction of catechols with halogeno-derivatives and subsequent oxidation of the hindered phenols formed:



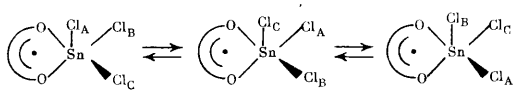
1. Pentacoordinate Chelate Complexes

The *o*-benzosemiquinone complex (XXVII) has been obtained by the reaction of tin tetrachloride with 3,6-di-t-butyl-*o*-benzoquinone (3,6-Q) [44] in toluene. Hyperfine coupling with two equivalent protons [$a_{H(4)} = a_{H(5)} = 3.9$ G], one $^{35,37}Cl$ nucleus ($I = 3/2$, $a_{Cl} = 0.6$ G), and the magnetic isotopes ^{117}Sn and ^{119}Sn ($a_{^{117}Sn} = a_{^{119}Sn} = 7.2$ G) has been recorded for this compound at room temperature. The spectroscopic data obtained led to the conclusion that the complex (XXVII) formed has a chelate tetragonal-pyramidal structure (see Fig.11*a*):[44]



(XXVII)

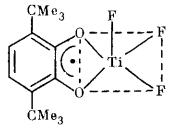
This structure explains why hyperfine coupling with only one chlorine nucleus was recorded: the other two lie near the nodal plane of the π orbital of the unpaired electron and hyperfine coupling with them is not manifested in the spectrum. With increase of temperature in the range 40–80 °C, the HFS lines are broadened due to the coupling with the chlorine nucleus and above 100 °C each component of the proton triplet is split into ten lines (Fig.11*b*) due to the hyperfine coupling with the three equivalent chlorine atoms ($a_{Cl} = 0.3$ G). The temperature-induced changes are fully reversible and indicate the presence of a dynamic effect due to the rotation of the $SnCl_3$ group relative to the plane of the *o*-semiquinone ligand at an elevated temperature. This rotation can be considered from the standpoint of the "tourniquet" mechanism proposed for compounds with a pentacoordinate phosphorus atom[45,46]:



As a result of such rotation, all three chlorine nuclei become equivalent and the constant for hyperfine coupling with the $^{35}Cl(^{37}Cl)$nuclei diminishes by a factor of 2 which is typical for hyperfine coupling with the β-nuclei in free radicals when the unpaired electron is delocalised via a hyperconjugation mechanism. The frequency of rotation in the range 20–50 °C has been estimated and is described by the expression[44]

$$\nu_{wt}(s^{-1}) = 2.4 \cdot 10^{15} \exp[-(13000 \pm 1000)/RT]; \nu_{rot}(20^\circ C) = 6 \cdot 10^5 s^{-1}.$$

The complex (XXVIII), obtained by the interaction of titanium tetrafluoride with 3,6-Q in toluene, has an analogous tetragonal-pyramidal structure[56]. Triplet splitting by two equivalent protons [$a_{H(4)} = a_{H(5)} = 3.8$ G], a doublet due to the ^{19}F nucleus, located outside the nodal plane ($a_{^{19}F} = 4.7$ G), and a narrow triplet due to two fluorine nuclei, located in the vicinity of the nodal plane ($a_F = 0.6$ G) (Fig.12) are recorded in this case.



(XXVIII)

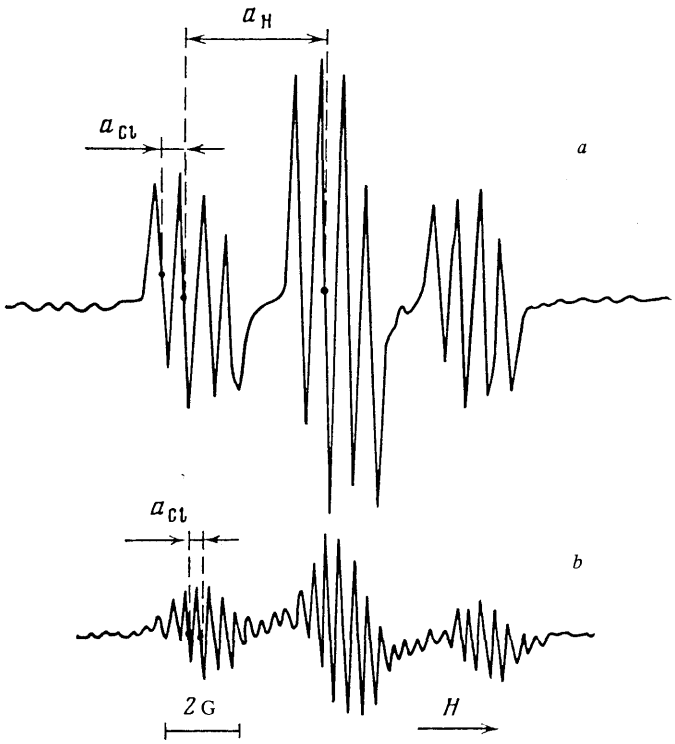


Figure 11. EPR spectrum of the complex (XXVII) in solution in toluene at 0 °C (*a*) and 100 °C (*b*).[44]

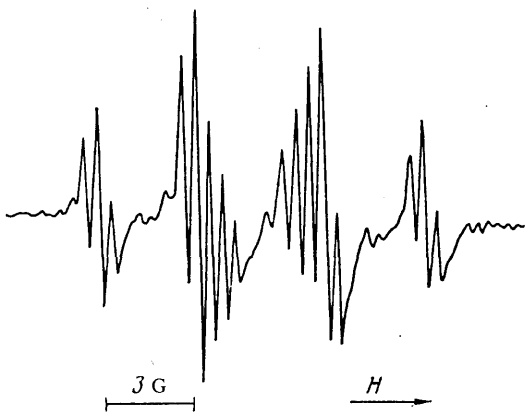


Figure 12. EPR spectrum of the complex (XXVIII) in toluene at 20 °C.[56]

The HFC constants (3.8 G) were assigned to two protons of the *o*-semiquinone ligand on the grounds that their sum [$a_{H(4)} + a_{H(5)} = 7.6$ G] is typical for organoelemental radicals with 3,6-di-t-butyl-1,2-dihydroxybenzene ligands. The greater magnetic moment of the ^{19}F nuclei compared with the $^{35}Cl(^{37}Cl)$ nuclei as well as the small size of the central atom compared with tin are responsible for the higher constants for the hyperfine coupling with these nuclei and also for the detection of the hyperfine coupling with the fluorine nuclei located in the vicinity of the nodal plane in this case. Over the entire temperature range (from -80° to 100 °C), the spectral pattern remains unchanged, which is apparently associated with the low frequencies of rotation of the TiF_3 groups relative to the plane of the catechol ligand[56].

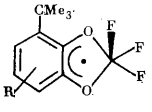
Hyperfine coupling with three nonequivalent nuclei having a spin of 1/2 (the HFC constants are 3.5, 4.2, and 4.9 G) and with the ^{117}Sn and ^{119}Sn nuclei has been recorded in toluene for the 3,6-di-t-butyl-*o*-semiquinone complex containing the SnF_3 group[55]. The HFC constants amounting to 3.5 and 4.2 G were assigned to the protons of the *o*-semiquinone ligand on the basis of their characteristic sum, which is 7.7 G.[47] Correspondingly, the HFC constant equal to 4.9 G was assigned to the ^{19}F nucleus located outside the nodal plane. Since two structures—a tetragonal pyramid and a trigonal bipyramid—are possible for the pentacoordinate tin compounds, the observed non-equivalence of the ring protons can be explained by the distortion of the former structure towards the latter structure with an apical equatorial disposition of the *o*-semiquinone ligand. On the other hand, the non-equivalence of the ring protons in the trigonal bipyramid reflects the non-equivalence of the apical and equatorial E–O bonds[48].

Table 5. The spectroscopic parameters (G) of the radicals (XXIX)–(XXXI) in toluene at 20 °C.[56]

Radical	$a_{H(4)}$	$a_{H(5)}$	a_F^a	a_F^e
(XXIX)	4.2	3.6	0.35 (2)	10.1 (1)
(XXX)	—	3.8	1.0 (2)	9.7 (1)
(XXXI)	—	3.8	—	9.9

Note: the number of fluorine atoms is indicated in brackets. $a_H = 0.4$ G for the hydrogen atoms of the t-butyl groups in the radical (XXX); a_F^a and a_F^e refer respectively to the apical and equatorial positions of the ligand.

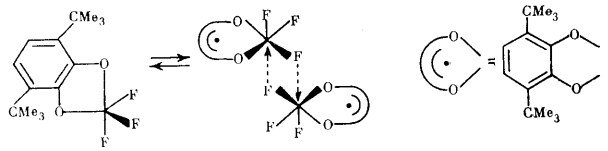
The structure of the trigonal bipyramid with an apical-equatorial disposition of the *o*-semiquinone ligand is characteristic of all the pentacoordinate silicon complexes which we investigated[49]. They were obtained by the reaction of SiF_4 with substituted *o*-quinones in weakly solvating media (toluene, ether). Table 5 presents the spectroscopic parameters for the complexes (XXIX), (XXX), and (XXXI) formed, on the basis of which it was concluded that they have a chelate trigonal-bipyramidal structure[56]:



(XXIX)–(XXXI)

where R = 6-t-butyl (XXIX), 5-t-butyl (XXX), or 5-trityl (XXXI). In this case the non-equivalence of the fluorine atoms is caused by their different steric dispositions relative to the nodal plane of the π orbitals of the unpaired electron. The non-equivalence of the ring protons of the 3,6-di-t-butyl-*o*-semiquinone ligand is caused by the non-equivalence of the apical and equatorial Si–O bonds in the trigonal bipyramid[49].

On reducing the temperature, spectroscopic changes were observed for the 3,6-di-t-butyl-*o*-semiquinone ligand, which can be explained by the association of the radical complexes (XXIX). This resulted in an alteration of the ratio of the constants for the hyperfine coupling with the ^{19}F nucleus and an additional hyperfine coupling (0.2 G), which we assumed to be due to the ^{19}F nucleus of another molecule of the complex, was recorded. The ring protons of the 3,6-di-t-butyl-*o*-semiquinone ligand then become equivalent:[50]



(XXIX)

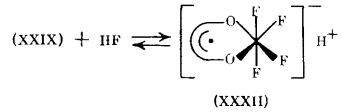
The spectra of the frozen solutions are characterised by an effective spin–spin interaction, which also confirms our hypothesis of the formation of associated species. On the basis of the zero splitting parameters obtained ($D = 316$ G, $E = 27$ G), the distance between the radical centres ($r = 4.4$ Å) was determined. The evolution of the spectra as a function of temperature is fully reversible.

Thus the coordination sphere of the central atom expands to six during the association process and there is a corresponding transition from the trigonal bipyramid to an octahedron, which is manifested spectroscopically by the appearance of a symmetrical distribution of the spin density (equivalent ring protons of the 3,6-di-t-butyl-*o*-semiquinone ligand) and the detection of hyperfine coupling with four fluorine nuclei.

Pentacoordinate tetragonal-pyramidal and trigonal-bipyramidal complexes of silicon, titanium, and tin exhibit electron-deficient properties and can coordinate additionally various electron-donating species (anions, solvent molecules) with formation of hexacoordinate octahedral radical-anions or molecular complexes.

2. Octahedral Chelate Complexes

In toluene which has not been carefully freed of moisture, the evolution of the spectra of the radical (XXIX) as a function of temperature differed significantly from that in dry toluene and corresponded to equilibrium between the radical (XXIX) and the radical-anion (XXXII) having an octahedral structure (Fig.13):[48]



(XXXII)

The change in the geometry of the complex from a trigonal bipyramid to an octahedron leads to the equalisation of the constants for the hyperfine coupling with the ring protons and the constants for the hyperfine coupling with the four ^{19}F nuclei, which are equal in pairs, are determined by their disposition relative to the nodal plane of the free-radical ligand. The evolution of the spectra as a function of temperature is fully reversible. The addition of diphenylamine or triethylamine to the reaction mixture fully displaces the equilibrium towards the radical-anion and the spectrum of

(XXXII) is recorded over the entire temperature range (up to 80 °C). Evidently the radical-anion complex is stabilised by the formation of an ammonium cation.

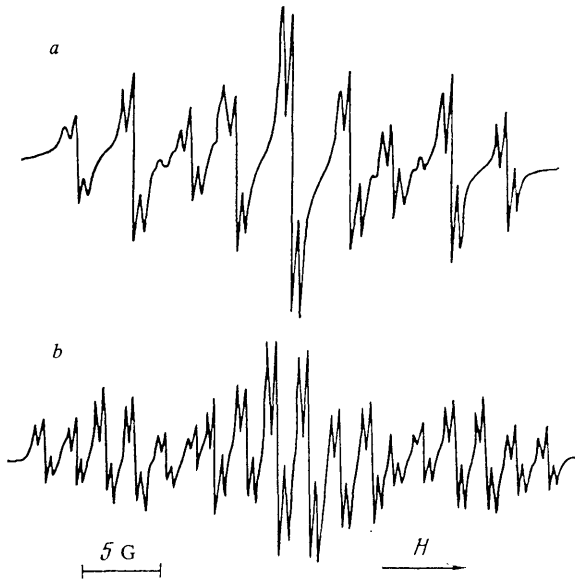
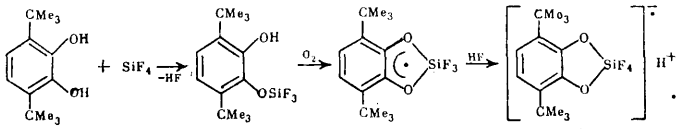
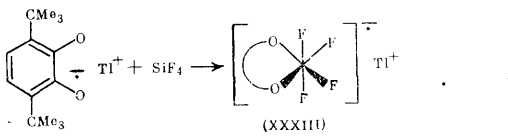


Figure 13. EPR spectra of the radical-anion (XXXII) (*a*) and its thallium salt (*b*) in toluene at 20 °C.[49]

When tetrafluorosilane interacts with 3,6-di-t-butyl-1,2-dihydroxybenzene, the EPR spectrum of the radical-anion (XXXII) is also recorded. Under the conditions indicated, the formation of large amounts of HF is apparently inevitable, which displaces the above equilibrium towards (XXXII):



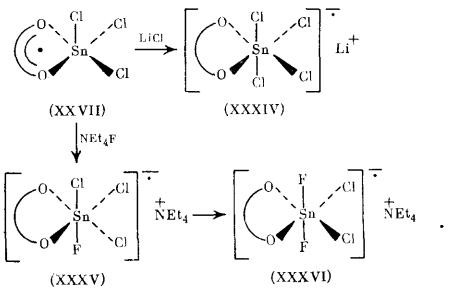
When thallium semiquinolate interacts with tetrafluorosilane, the corresponding thallium salt (XXXIII) is formed and the splitting due to the ^{203}Tl and ^{205}Tl nuclei (a_{Tl} = 2.1 G) is recorded (Fig. 13*b*):



(XXXIII)

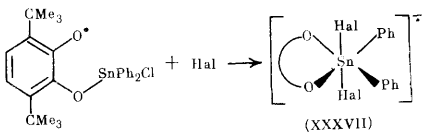
The 3,6-di-t-butyltrifluorostannyl-*o*-semiquinone complex forms analogous salts in moist toluene as a result of the formation of HF during the reaction. Hyperfine coupling with the four nuclei, equivalent in pairs and having a spin of 1/2, is then recorded, two signals referring to the ring protons (a_H = 3.8 G) and the other two to the ^{19}F nuclei located outside the nodal plane of the free radical ligand (a_F = 4.2 G).

Tin-containing complexes of the radical-anion type [the complexes (XXXIV), (XXXV), and (XXXVI)] have been obtained also by the addition of lithium halides in the presence of crown-ether and tetraethylammonium to a toluene solution of the complex (XXVII):



(XXVII) (XXXIV) (XXXV) (XXXVI)

Hyperfine coupling with the two equivalent ring protons of the *o*-semiquinone ligands, the halogen nuclei located outside the nodal plane, and the ^{117}Sn and ^{119}Sn nuclei is detected in the EPR spectra of the complexes (XXXIV) to (XXXVI). Complexes of an analogous type [the complexes (XXXVII)] arise also when the 3,6-di-t-butyldiphenylchlorostannyloxyphenoxy-radical, where the coordination number is in essence four, is treated with the same salts[51]:



(XXXVII)

where Hal = Cl^- (XXXVIIa) or F^- (XXXVIIb).

Table 6 lists the spectroscopic parameters of the radical-anionic complexes obtained. In the instance indicated above, the transformation of a typical phenoxy-radical into an octahedral chelate complex can be seen. This transition as well as the equalisation of the lengths of the Sn–O bonds apparently take place as a result of the intramolecular charge transfer to the univalent oxygen atom from the central atom which is electronically saturated by the additional halide anion. After treating the 3,6-di-t-butyl-2-triphenylstannyloxyphenoxy-radical with salts, we were unable to detect the formation of radical-anionic complexes. This shows that the stability of the octahedral radical-anionic complexes is determined by the electron deficit of the central atom, which depends in its turn on the number of halogen atoms bound to it[52].

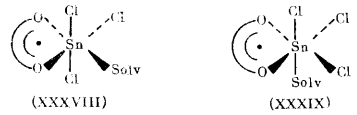
Table 6. The spectroscopic parameters (G) of the radical-anionic complexes of tin with the 3,6-di-t-butyl-1,2-dihydroxybenzene ligands in toluene at 20 °C.[51]

Complex	$a_{H(1)=a_{H(5)}}$	$a_{^{35,37}Cl}$	a_F
(XXXIV)	3.6	0.6 (2)	—
(XXXV)	3.7	0.6 (1)	4.1 (1)
(XXXVI)	3.7	—	4.0 (2)
(XXXVIIa)	3.7	0.6 (2)	—
(XXXVIIb)	3.7	—	4.0 (2)

Note: $a_{^{117,119}Sn}$ = 6.0 G for all the complexes indicated; the number of chlorine or fluorine atoms respectively is indicated in brackets.

Electron-donating molecules can also form complexes with pentacoordinate compounds of Group IV elements. It follows from the analysis of their EPR spectra that the coordinated molecule can be located either in the plane of

the *o*-semiquinone ligand or outside it. Thus the complex (XXVII) can give rise to one of the structures indicated below depending on the nature of the ligand entering it[44]:

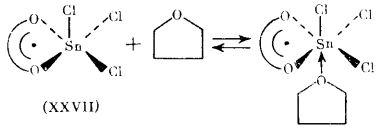


(XXXVIII) (XXXIX)

Solv = CH_3COCH_3, CH_3CN, DMF Solv = $P(O)R_3$, THF

Hyperfine coupling with two $^{35}Cl(^{37}Cl)$nuclei (apart from the hyperfine coupling with the equivalent ring protons) is detected in the spectra of the complexes (XXXVIII) and hyperfine coupling with a single $^{35}Cl(^{37}Cl)$nucleus is detected in the spectra of structure (XXXIX). For complexes where a phosphate molecule is coordinated to the central atom, additional splitting by the ^{31}P nucleus, amounting to approximately 0.2–0.4 G, is detected, which confirms the coordination of the phosphate outside the plane of the free-radical ligand. These complexes are extremely stable and the form of the spectra does not change over a wide temperature range (up to 100 °C).

A complex of type (XXXIX) with THF, which is in equilibrium with the initial complex (XXVII) and free THF, is an exception:



(XXVII)

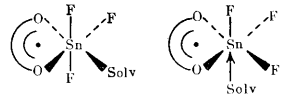
The spectra of the free complex (XXVII) and the complex solvated by THF molecules have the same hyperfine structure, but their *g*-factors differ somewhat. Analysis of the line intensities of both species made it possible to estimate the thermodynamic parameters of the above equilibrium: K_p(20 °C) = 0.23 litre mol^{-1}, ΔH = 4.1 kcal mol^{-1}, and ΔS = −14 e.u.

Table 7. The spectroscopic parameters (G) of the 3,6-di-t-butyl-*o*-semiquinone complex containing the trifluorostannyl group in various solvents at 20 °C.[56]

Solvent	α	$a_{H(4)}$	$a_{H(5)}$	a_F	a_F	$a_{^{117}Sn}$	$a_{^{119}Sn}$
Diethyl ether	0.6	4.1	3.6	4.1	4.1	13.4	14.0
		3.9	3.9	4.4	—	11.9	12.3
THF	0.3	4.1	3.6	4.1	4.1	12.8	13.5
		3.9	3.9	4.4	—	12.5	13.2
Acetone	0.1	4.2	3.7	4.2	4.2	13.2	13.8
		3.9	3.9	4.6	—	14.2	14.8
Acetonitrile	0.03	4.1	3.6	4.1	4.1	13.0	13.4
		3.9	3.9	4.6	—	13.2	13.7
Ethanol	0.3	3.8	3.8	4.4	4.1	12.5	12.5
		3.8	3.8	4.7	—	12.8	12.8

Note: the spectroscopic parameters of the complexes (XXXVIIIa) and (XXXIXa) are quoted for each solvent in the upper and lower row respectively; α is the ratio of the mole fractions of the complexes (XXXIXa) and (XXXVIIIa).

The simultaneous existence of complexes of types (XXXVIII) and (XXXIX) has been detected in the EPR spectra of trifluorostannyl complexes with the 3,6-di-t-butyl-*o*-semiquinone ligand in polar solvents. The spectroscopic parameters of these complexes are presented in Table 7, which also lists the ratios of the mole fractions of these forms: α = [(XXXVIII)]/[(XXXIX)].



(XXXVIIIa) (XXXIXa)

The non-equivalence of the ring protons in the form (XXXVIIIa) is due to the slight distortion of the octahedral structure. It is noteworthy that, for measurements in ethanol, the spectroscopic parameters of the form (XXXVIIIa) indicate the absence of distortion of the octahedral configuration. The relative line intensities of the EPR spectra assigned to these forms are independent of temperature, which is apparently associated with the similar thermodynamic stabilities of the two forms.

The molecular octahedral complex formed following the addition of acetylacetone to a toluene solution of the radical (XXIX) (acetylacetone : toluene = 1 : 1), is of interest. The fluorine is substituted in this instance by the acetylacetonate ligand which, being bidentate, occupies two coordination sites in the sphere of the central silicon atom, which leads to the formation of the complex (XL) whose EPR spectrum and structure are illustrated in Fig. 14.

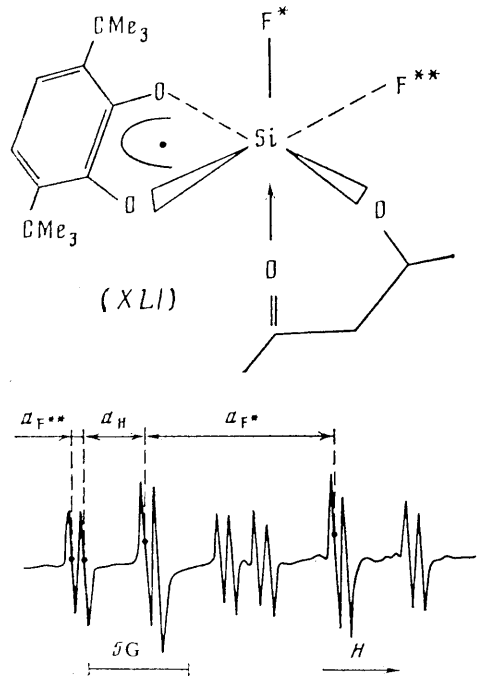
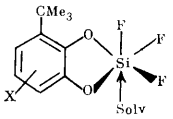


Figure 14. EPR spectrum and structure of the complex (XL) (toluene : acetylacetone = 1 : 1) at 20 °C.[56]

The interaction of SiF_4 with substituted *o*-quinones in solvating solvents—THF, dimethoxyethane (DME), and acetonitrile—yielded *o*-semiquinone complexes whose spectroscopic parameters (Table 8) correspond to an octahedral configuration in which one site outside the plane

of the free-radical ligand is occupied by the solvent molecule (Solv):[50]



(XLI)-(XLIII)

where X = 6-t-butyl (XLI), 5-t-butyl (XLII), or 5-trityl (XLIII). The unexpectedly high constants for hyperfine coupling with the ^{19}F nuclei located in the vicinity of the nodal plane of the free-radical ligand in the complexes (XLII) and (XLIII) are apparently caused by the distortion of the octahedral structure towards a trigonal pyramid as a result of the low symmetry of the *o*-semiquinone ligands.

Table 8. The spectroscopic parameters (G) of the radicals (XLI)–(XLIII) in tetrahydrofuran at −70 °C.[53]

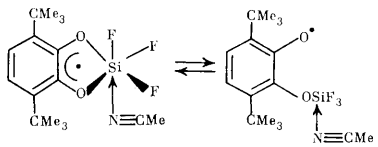
Radical	$a_{H(4)}$	$a_{H(5)}$	a_F	$a_{F'}$
(XLI)	4.1	4.1	0.72 (2)	9.4 (1)
(XLII)	—	4.0	5.50 (2)	9.0 (1)
(XLIII)	—	4.0	5.40 (2)	9.4 (1)

Note: a_F and $a_{F'}$ are the constants for the hyperfine coupling with the fluorine nuclei near and outside the nodal plane of the free-radical ligand. The number of fluorine atoms is indicated in brackets. The constant for the hyperfine coupling with the protons of the t-butyl group in (XLII) is $a_H = 0.5$ G.

The evolution of the EPR spectra of the complex (XLI) as a function of temperature corresponds to the hindered rotation of the trifluorosilyl group relative to the plane of the *o*-semiquinone ligand (Fig. 15): at −70 °C hyperfine coupling with three non-equivalent ^{19}F nuclei is detected, while above 30 °C all three ^{19}F nuclei become equivalent ($a_F = 3.2$ G).[53] Analysis of the line widths in the spectra corresponding to slow exchange made it possible to estimate the rotation frequencies of the SiF_3 group:

$$\nu_{rot}(s^{-1}) = 7\cdot10^{13}\exp[-(6200\pm1000)/RT];\ \nu_{rot}(20\,^{\circ}C) = 1.7\cdot10^{9}\ s^{-1}.$$

The mechanism of the hindered rotation can be intermolecular in this instance due to the decomposition of the complex (XLI) and the formation of the complex (XXIX). In the subsequent coordination, a THF molecule can add from the other side, whereupon the relative disposition of the fluorine atoms and the THF molecule can be different. One cannot rule out the possibility that the ligand exchange can be synchronous, i.e. can proceed without the formation of the complex (XXIX). An analogous spectral pattern has been recorded in DME. The spectral changes in acetonitrile at low temperatures (up to 0 °C) also correspond to the hindered rotation of the SiF_3 group. Above 0 °C, the chelate ring opens and the corresponding phenoxy-radical with the trifluorosiloxy-group in the *o*-position is formed. The ring protons then become non-equivalent [$a_{H(4)}$ = 4.0 G, $a_{H(5)}$ = 2.6 G]; on the other hand, the constants for the hyperfine coupling with the ^{19}F nuclei are equalised and greatly diminish ($a_F = 1.7$ G); furthermore, an additional splitting by the ^{14}N nucleus ($a_N = 4.0$ G) of the solvent molecule is detected:



(XLIV) (XLV)

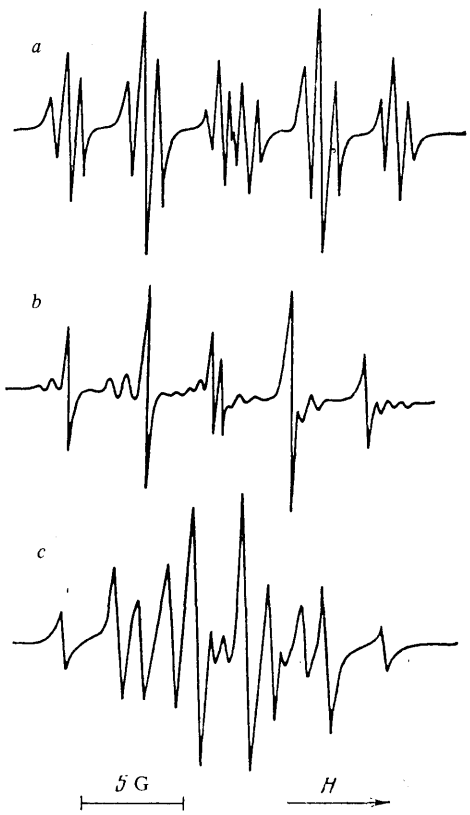
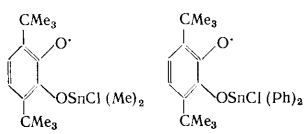


Figure 15. EPR spectra of the complex (XLI) in THF at different temperatures (°C): *a*) −70; *b*) −30; *c*) 30.[53]

The chelate complex (XLIV) can be converted into the phenoxy-radical (XLV) also when the electronegativity of the substituents at the central atom is reduced. Thus, after the replacement of two chlorine atoms in the complex (XXVII) by methyl or phenyl substituents, the chelate complex is converted into the phenoxy-radicals (XLVI) and (XLVII) respectively:



(XLVI) (XLVII)

* *

*

The examples presented show that the application of the EPR and electronic absorption spectroscopic methods to the study of variable-valence metal complexes of *o*-quinones makes it possible to establish the electronic structure of the complexes and to elucidate the wide variety of electronic configurations permitted by the nature of the *o*-benzoquinone ligands.

Analysis of a large number of experimental constants for hyperfine coupling with the magnetic nuclei forming part of the composition of the ligands in the paramagnetic *o*-quinone complexes of Group IV elements permits a conclusion concerning the geometrical structures of the complexes and about the alteration of the latter following the coordination of new ligands, which is of general interest for the chemistry of coordination compounds.

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Nesmeyanov Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 518-539 (1984) U.D.C. 678.769

Oligomers and Polymers with Reactive Acetylenic Groups

V.A.Sergeev, Yu.A.Chernomordik, and A.S.Kurapov

The problem of the synthesis and study of the properties of thermoreactive oligomers and polymers containing reactive acetylenic groups, leading to the formation of compounds with a three-dimensional structure, are examined. Pathways leading to the formation of oligomers and polymers from acetylenic monomers during their polycyclotrimerisation with retention of the residual acetylenic groups as well as the methods of synthesis of various oligomers and polymers with subsequent introduction of acetylenic groups into the latter are indicated. The possible structural transformations of the acetylenic groups during the hardening process with formation of rigid and cross-linked polymers without the evolution of volatile products are discussed. The bibliography includes 126 references.

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I. INTRODUCTION

The problems of the synthesis of oligomers and polymers with acetylenic bonds and of the preparation of materials based on them has recently been attracting increasing attention. This can be explained by the likely usefulness of acetylenic compounds for the preparation of reactive oligomers and polymers and heat resistant and thermostable materials based on them. The acetylenic group is being successfully used nowadays in various classes of thermostable polymers: polyphenylenes and carbochain polymers, polyethers and polyesters, polyamides, polyurethanes and other heterochain compounds, and polymers with a heterocyclic structure: polyimides, polyphenylquinoxalines, polydibenzoxazoles, etc.

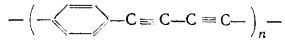
The use of the acetylenic group in the synthesis of polymers has led to considerable progress in the chemistry and technology of materials based on the polymers enumerated above. In the first place mention should be made of the decreased processing temperature, the improved solubility and fluidity of the starting materials, the possiblity of obtaining large components, and an improvement in the quality of the articles. One of the first polymers of acetylene has been "cuprene" obtained at the end of the last century by passing acetylene through a copper tube heated to 240–250 °C.[1] It did not find practical applications.

At the end of the 1960s Korshak and co-workers[2,3] achieved the polymerisation of a number of acetylenic compounds under pressure. Phenylacetylene and propargyl alcohol were polymerised and polymers with a system of conjugated double bonds were obtained. In a number of other studies[4,5], various monomers were subjected to catalytic and radiation-induced polymerisation. These investigations indicated ways of employing the acetylenic group in polymer synthesis and revealed the possibility of stabilising many polymers by binding the free radicals formed on decomposition of the polymer.

Oligomers and polymers containing acetylenic groups were first obtained by Korshak and co-workers[6,7] and also by Kotlyarevskii et al.[8] by the oxidative dehydropolycondensation of acetylenic monomers. Thus, "carbyne"—a polymer with triple carbon–carbon bonds in the chain which constitutes a new linear modification of carbon—was obtained from acetylene by this reaction; it is a black powder capable of being converted into graphite at 2300 °C.[7] The carbyne formation reaction can be represented schematically in a general form as follows:

$$n\,HC{\equiv}CH \xrightarrow{[O]} (-C{\equiv}C-)_n- \quad .$$

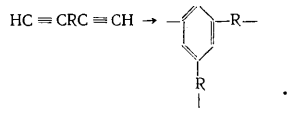
Polyacetylene having the structure



has been obtained from *p*-diethynylbenzene. The study of polyacetylenes showed that they possess semiconducting properties and exhibit photoconductivity.

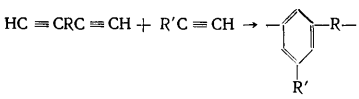
The specific synthesis of carbyne has been achieved[9] by the dehydrochlorination of poly(vinylidene chloride).

The polymerisation and oxidative dehydropolycondensation reactions of acetylenic monomers lead to the formation of linear polymers. At the end of the 1960s and the beginning of the 1970s Korshak and co-workers[10,11] developed a funamentally new method of synthesis of polymers with acetylenic groups by the polycyclotrimerisation of acetylenic compounds in which aromatic carbocycles are formed as a consequence of the interaction of three acetylenic groups and their closure to form a six-membered ring in accordance with the scheme



However, certain difficulties arise in carrying out this process with a high degree of selectivity, because all the monomers used for the polycyclotrimerisation can just as readily polymerise with the parallel formation of other unity in the chain, which is undesirable from the standpoint of the polycyclotrimerisation process. In order to carry out the polycyclotrimerisation reaction, it is necessary that at least one of the monomers involved in the process should contain two acetylenic groups. The polycyclotrimerisation reaction is usually performed in the presence of a catalyst[12–15] whose efficienty largely determines the selectivity of the process.

The joint polycyclotrimerisation in accordance with the scheme

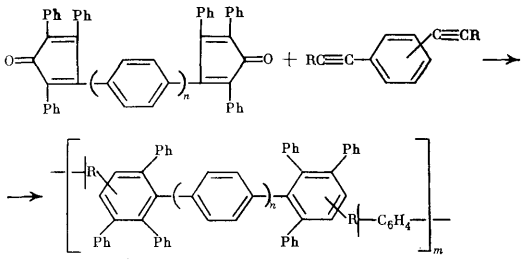


is of greatest practical interest. This reaction is based on the use of acetylenes and their derivatives and does not lead solely to the formation of polyphenylenes having various structures and containing reactive groups. The most interesting are the oligophenylenes containing residual triple bonds as functional groups, because this facilitates the subsequent, chemical modification and hardening of the polymers. The polycyclotrimerisation process makes it possible to regulate the content of the triple bonds in the polymer[15-18].

The above possibilities of the polycyclotrimerisation reaction have attracted in recent years much attention by investigators working in the field of the synthesis of polymers both in our country and abroad. A review was published in 1980 [19] which attempted to extend the fundamental approach to the introduction of the acetylenic linkage into an oligophenylene, developed by Soviet workers[20], to other classes of polymers. The studies initiated by Korshak and co-workers[10] on the polycyclotrimerisation of acetylenic compounds were subsequently extended by the same investigators to the polycyclotrimerisation of dinitriles and dicyanoesters; on this basis, a general method was developed for the synthesis of polymers[21,22], their modification, and the formation of three-dimensional networks.

Before the publication of the studies by Korshak and co-workers, isolated communications on the problems of the synthesis of acetylene-containing polyphenylenes could be found in the literature. Thus the Diels–Alder reaction of bistriphenylcyclopentadienones with diacetylenes in accordance with the scheme

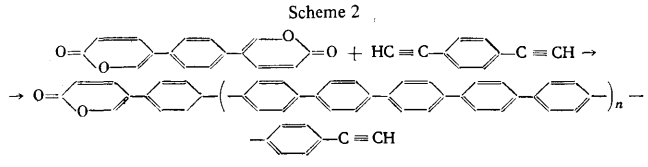
Scheme 1



has been described[23,24]. In the presence of more than a twofold excess of acetylene, the resulting polymer could contain acetylenic groups at the ends of the macromolecule.

The reaction of bispyrones with diacetylenes[24] via the scheme

Scheme 2



proceeds analogously.

At attempt has been made to obtain aromatic polymers from non-conjugated diacetylenes[26]. However, the oligomers synthesised consisted mainly of polymers having a polyene structure with small amounts of admixtures of dimers and trimers having indan, cyclophane, and arylacetylene structures.

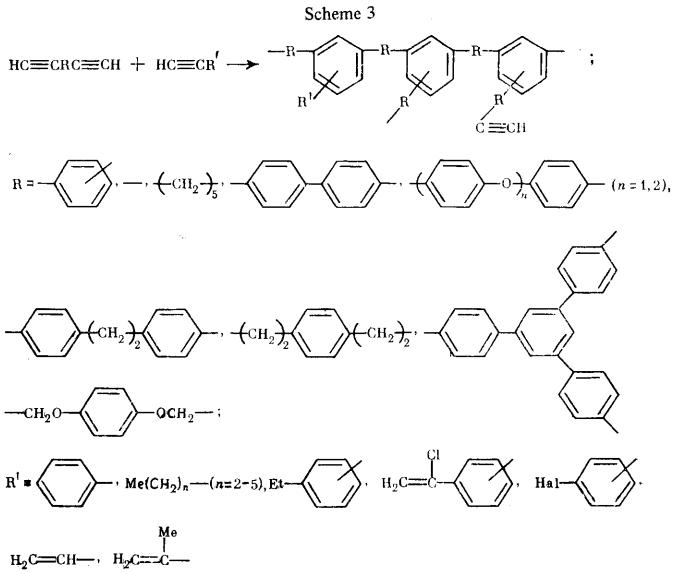
Extensive data have now accumulated on the problem of the synthesis and study of the structures and properties of oligomers and polymers containing reactive acetylenic groups; examination and survey of these data is the aim of the present review.

II. CARBOCHAIN OLIGOMERS AND POLYMERS

1. Polyphenylenes

One of the most common methods of synthesis of oligophenylenes with acetylenic groups is the polycyclotrimerisation of diethynylcompounds or their mixtures with monoethynyl compounds. The possibility of carrying a selective process under relatively mild conditions has been noted[10,27,28]. A series of syntheses in accordance with the scheme

Scheme 3



were carried out.

p-Diethynylbenzene and phenylacetylene have acquired the greatest importance as the diethynyl and monoethynyl compounds respectively. The polycyclotrimerisation reaction is usually accompanied by the conversion of the acetylenic compounds into polyenes. The catalysts of such a mixed process may be $[(EtO)_3P]_4CoBr$, $NiCl_2.2PPh_3.2NaBH_4$, and also Ziegler catalysts[20]; it has been shown that the last are the most effective and that in their presence (for specific ratios of AlR_3 and $TiCl_4$) the polycyclotrimerisation reaction becomes dominant. The oligophenylenes obtained with molecular weights in the range 1000–5000 readily dissolve in benzene, toluene, and chlorinated organic solvents.

The study of the thermal properties of the products showed that they are readily hardened[10] at temperatures in the range 150–250 °C and that the hardening process is completed at 300–350 °C. Oligophenylenes containing residual ethynyl groups are therefore capable of producing polyphenylenes with a high deformation thermal stability, the latter increasing with the number of ethynyl groups in the initial oligophenylene. The properties of the oligophenylene depend on the structure of the initial monomers, on the reaction conditions, on the type and composition of the catalyst, and the ratio of the initial monoethynyl and diethynyl monomers, etc. Certain methods of synthesis and properties of the oligophenylenes were described previously in reviews[29,30] and here we shall deal with the main new investigations.

The mechanism of the polycyclotrimerisation reaction of acetylenic compounds was investigated by statistical and thermodynamic methods and also a number of other procedures[15,16,29–36] and it was concluded that the reaction involves stepwise coordination polyaddition which differs from both polymerisation and polycondensation and is a new reaction leading to the synthesis of polymers. As a consequence of the coordination character of the process, the structure and properties of the oligomers obtained depend on the structure of the initial monomers and in the first place on the flexibility or rigidity of the interethynyl diacetylene fragment[37–40] and on steric factors[17,18,36,41], because they determine the nature of the preliminary orientation of the acetylenic molecules in the formation of the aromatic ring on the catalytic complex. The stepwise, discrete character of the process is responsible for the additivity of the influence of the ratio of the diethynyl and monoethynyl monomers, of the order of the introduction of the monomers, and of other reaction conditions on the structure and properties of the polyphenylenes[18,42–44].

The reaction mechanism was inferred with the aid of the statistical theory of branching processes based on the cascade theory[15,16,39,40,45,46]. The structure of the oligophenylenes was investigated by the method of ozonolysis[47]; it was shown that the polycyclotrimerisation of acetylenic compounds in the presence of the $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$ catalytic system is a highly selective process and the influence of the polyene sections has almost no effect as a consequence of their small amount.

Taking into account the characteristics of the polycyclotrimerisation reaction, polymers with properties useful in practice, namely thermostable and mechanically strong polymers, were synthesised specifically from phenoxyacetylenes[38,48,49]. Thus, as a consequence of the presence of oxygen "hinge" atoms between the benzene rings, the polymers based on di(4-ethylphenyl) ether and 1,4-di(4-ethynylphenoxy)benzene produced specimens which are more easily worked than oligophenylenes based on *p*-diethynylbenzene and have high moduli of elasticity and high compressive strengths (reaching 1000–1400 kg cm^{-2} compared with 350 kg cm^{-2} for oligophenylenes based on *p*-diethylbenzene); the limiting deformation of these polymers without rupture and their thermal stability and heat resistance were also higher. According to thermogravimetric data, intense weight losses are observed in an inert atmosphere in the temperature range 450–600 °C.[48]

In order to modify the properties of the oligomers, oligophenylenes based on various diethynyl, triethynyl, and monoethynyl monomers were synthesised: diphenyl butadiyne[50], 4,4′-diethynylbiphenyl[48], di(4-ethynylphenyl)ethane[37], diethynyltetraphenyldisiloxane[51], vinyl- and isopropenyl-acetylenes[52,53], chlorovinylphenylacetylene[42], ethylphenylacetylene[54], tri(ethynylphenyl)benzene[41] and other triethynyl compounds.

In order to increase the thermal stability of the polymer by increasing the number of unsaturated groups in the oligophenylene and in order to be able to employ the latter as a cross-linking agent, branched oligophenylenes with double bonds were synthesised[52,53] by the partial or complete replacement of phenylacetylene (in its copolycyclotrimerisation reaction with *p*-diethynylbenzene) by alkenylacetylenes: binylacetylene or isopropenylacetylene. The reaction was carried out at −10 °C in the presence of $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$, which is the most effective catalyst of the trimerisation of alkenylacetylenes[55,56]. In view of the ready structure formation in oligophenylenes with vinyl groups, a product fully soluble in organic solvents was obtained only on the basis of the ternary copolymer of *p*-diethynylbenzene, phenylacetylene, and vinylacetylene. The possibility of regulating the number of unsaturated groups in the ternary copolymers by varying the ratio of the initial components was demonstrated.

Oligophenylenes containing vinyl chloride groups have been synthesised[42]. During the preparation of *p*-diethynylbenzene from technical divinylbenzene, ethynyl(chlorovinyl)benzene remains in the reaction products as a consequence of the incomplete dehydrochlorination; it is difficult to remove completely. In order to elucidate the influence of this group on the polycyclotrimerisation product and to determine the possibility of achieving the synthesis from unpurified *p*-diethynylbenzene, the study mentioned above[42] was undertaken.

It was established that, when *p*-diethynylbenzene, phenylacetylene, and ethynyl(chlorovinyl)benzene interact, an oligomer with an increased degree of saturation of the bonds is formed as a result of the retention of the vinyl chloride group during the reaction. It was shown that phenylacetylene is more reactive towards *p*-diethynylbenzene than ethynyl(chlorovinyl)benzene. The chlorine atom in ethynyl(chlorovinyl)benzene apparently reduces (as a consequence of the inductive effect) the electron density in the triple bond of the acetylenic group relative to the electron density of the triple bond of phenylacetylene. The use of triethynyl monomers greatly improves the thermal stability of the polymers formed, whose softening temperature is in the region of intense thermal decomposition, i.e. above 500 °C.[41]

A polyphenylene and an oligophenylene have been synthesised from diacetylene and substituted acetylenes have been obtained by the polycyclotrimerisation reaction in solution in toluene at −10 °C in the presence of $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$.[17,43,57]. Both synthetic diacetylene, obtained by chlorinating butynediol with thionyl chloride and subsequent dehydrochlorination by alcoholic alkali, and pyrolytic diacetylene, which is a side product in the synthesis of acetylene from natural gas, were employed in the reaction. It was shown that an aromatic polymer is formed from initial monomers without benzene rings. In the polymer obtained from diacetylene alone, each aromatic ring is formed as a result of the interaction of three diacetylene molecules. The polymer is an amorphous yellow powder containing aromatic and ethynyl groups; it softens at 150–200 °C and hardens (owing to the presence of residual ethynyl end groups) on heating; in the cross-linked state, it exhibits a high thermal stability. According to thermogravimetric data, intense weight losses are observed in air at 400–600 °C.[43]

The high chemical stability of polyphenylenes and graphite-filled plastics based on them has been demonstrated[58]. Chemically stable polymeric materials used as binders and impregnating substances in industry include furan and phenol-formaldehyde resins and compositions based on them; however, they are stable only in relation to a 70% solution of sulphuric acid. Polyphenylenes and graphite-filled plastics exhibited an effective chemical stability in relation to an 80% solution of sulphuric acid at its boiling point (120–125 °C) for 850 h and also in relation to a 93% solution of sulphuric acid. The high thermal and corrosion stabilities of polyphenylene, which can be explained by its aromatic structure, make it a promising material as a binder in the preparation of graphite-polymeric materials.

The use of the products of the copolycyclotrimerisation of *p*-diethynylbenzene and a halogenophenylacetylene showed[44] that the reactivity of *p*-diethynylbenzene is somewhat higher than that of the halogeneophenylacetylene; the oligomers are therefore enriched in *p*-diethynylbenzene fragments compared with the initial mixture.

The capacity of oligophenylenes for structure formation under the influence of ultraviolet irradiation has been studied[48,60]. It has been suggested that, in the absence of oxygen, the photoinitiated cross-linking takes place via the

residual ethynyl end-groups, as in thermal cross-linking in an inert atmosphere. In the presence of oxygen, the rate of cross-linking increases as a consequence of the oxidation of the ethynyl groups to peroxy-groups and the decomposition of the latter with subsequent recombination of the radicals. The mechanism of the photochemical cross-linking of polyphenylenes by diazides has also been described[60].

The oligophenylenes obtained by the polycyclotrimerisation reaction are characterised by the presence of residual ethynyl groups which can enter into various reactions: they can be oxidised to carboxy-groups[12], can combine with decaborane[61] to form oligophenylenecarbaboranes, and can interact with diazo-compounds[62] to form oligophenylenepyrazoles. The oligomers obtained have acquired new functional groups, which expands the synthetic possibilities in polymer chemistry.

An oligophenylenecarbaborane has been synthesised by the chemical modification of an oligophenylene containing acetylenic end-groups under the influence of decaborane[61]. It was established that, under the chosen conditions, the replacement of the ethynyl groups of the oligophenylene by carbaborane groups takes place almost quantitatively via the scheme

$$B_{10}H_{14} + PhNMe_2 \rightarrow B_{10}H_{12}(PhNMe_2)_2 \xrightarrow{HC\equiv C-} HC(B_{10}H_{10})C- + PhNMe_2 + H_2 .$$

This demonstrated that the polycyclotrimerisation of ethynyl compounds in the presence of $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$ leads to the formation of oligphenylenes containing only aromatic units and residual triple bonds, which are responsible for the acquisition of a three-dimensional structure by the oligophenylene.

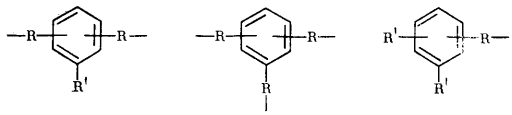
Oligophenylenepyrazoles have been obtained as a result of the modification of an oligophenylene having terminal ethynyl groups on treatment with diazomethane and bisdiazohexane and some of their properties, particularly their resistance to thermo-oxidation, have been estimated[62]. The ethynyl groups of oligophenylenes have been hydrosilyated by dihydrosilanes in order to improve their mechanical characteristics[63].

Oligophenylenes based on the dipropargyl ethers of hydroquinone and dian have been obtained recently together with phenylacetylene in the presence of cobaltocene as the catalyst[64]. The polymers exhibit an enhanced fluidity and fusibility and possess effective mechanical characteristics.

A wide range of acetylenic compounds capable of undergoing polycyclotrimerisation and copolycyclotrimerisation have been enumerated[65,66] and the importance of using effective catalytic systems has been discussed. The authors of these studies point out that many transition metal compounds used as the catalysts of the polymerisation of monoacetylenes cannot be used for polycyclotrimerisation. For example, nickel chloride in the presence of sodium tetrahydroborate leads to the formation of thermally unstable polyolefins and not aromatic structures in the polymerisation of phenylacetylene. The catalyst $Ni(CO)_2(PPh_3)_2$, which has been widely used for the polymerisation of acetylenes, leads to the formation of unsaturated linear trimers as well as trisubstituted benzenes. The reaction of phenylacetylenes and diethynylbenzene in the presence of this catalyst leads to the formation of polymers in the infrared spectra of which a band appears at 965 cm^{-1}, characteristic of a *trans*-substituted terminal double bond, which indicates the occurrence of linear polymerisation. The copolymerisation of phenylacetylene and *p*-diethynylbenzene in the presence of the carbonylphosphinenickel complex leads to the formation mainly of polyolefins instead of the required thermostable polyphenylenes.

When the $AlEt_2Cl$–$TiCl_4$ Ziegler catalyst is used under the conditions of its effective operation, only triphenylbenzene is formed from phenylacetylene, while high-molecular-weight polyphenylene polymers can be obtained by copolymerisation. The authors[65,66] believe that the main cause of the formation of polyphenylenes rather than polyolefins is the molar ratio Al/Ti = 1.5–5.0. They believe that the catalyst concentration can vary within wide limits but the molar ratio of the catalyst to the acetylene-containing monomers must be at least 1 : 300–1500. Chemical study of the reaction products demonstrated the absence of unsaturated double and triple bonds from the polymer. Taking these findings into account, it was established on the basis of infrared, ^1H NMR and, ^{13}C NMR spectroscopic data that the polymer contains only aromatic structures.

However, the absence of terminal acetylenic groups from the reaction products (polyphenylenes) precludes their modification; such polymers are hardened thermally at high temperatures via secondary processes involving the degradation of the oligophenylenes and the recombination of radicals. The authors[65,66] introduced the monoacetylene monomer (phenylacetylene or tolylacetylene) into the reaction with diethynylbenzene in portions, which they believe to ensure a high solubility of the resulting polymer. They suggest that the reaction proceeds via three different pathways: chain propagation, chain branching, and chain termination, to which correspond three different types of fragments.

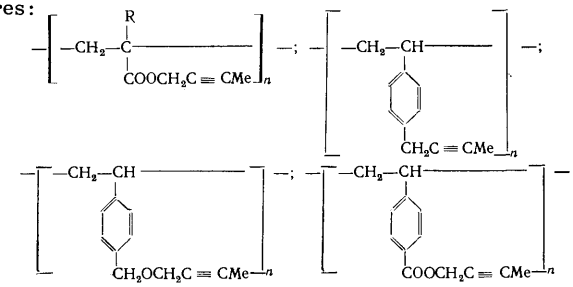


The synthesis of a polyphenylene containing residual ethynyl groups has been described[67]. Only one component, namely *p*-diethynylbenzene, was used for its synthesis; the reaction was carried out in the presence of two different catalytic systems: diethylaluminium chloride and titanium tetrachloride and nickel acetylacetonate. The authors[67] point out that the polyphenylenes which they obtained were soluble in organic solvents up to high degrees of conversion of the monomer into the polymer. For the Ziegler type catalyst, this claim conflicts with data[66] according to which a soluble polyphenylene cannot be obtained from diethynylbenzene alone.

2. Carbochain Polymers

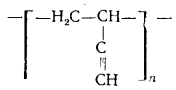
Carbochain polymers with a linear structure have been obtained, as already stated, by the oxidative dehydropolycondensation reaction[7]. By treating the polymers obtained with bistetraphenylcyclopentadienone, it is possible to increase their thermal stability and to employ them as binders, films, and coatings.

Carbochain polymers containing acetylenic groups in the side chain have been synthesised by the polymerisation of vinyl monomers[68–70] and were found to have the following structures:



Polymers of this type, soluble in organic solvents at elevated temperatures (120 °C and above), were cross-linked. It was established that the non-cross-linked polymers can combine with bromine and decaborane at the triple bonds.

Polymers with an unsubstituted acetylenic group in the side chain have also been synthesised[71]. A polymer with a triple bond linked directly to the main chain could not be obtained from a polyolefin. A polyconjugated polymer containing vinyl, allene, and acetylenic groups is formed in this case. In order to obtain a polymer containing an ethynyl side group of the type

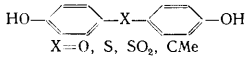


trimethylsilylvinylacetylene is usually polymerised with subsequent removal of the trimethylsilyl group.

III. HETEROCHAIN OLIGOMERS AND POLYMERS

1. Polyethers and Polyesters

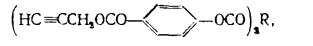
Polyethers have been obtained by the thermal polymerisation of di(4-ethynylphenyl) ether on heating to 150 °C.[72] The polymer obtained was used as a binder for composite materials. The kinetics of the thermal polymerisation of 3-ethynylphenyl phenyl ether have been investigated[73]. By treating bisphenols having the general formula



X=O, S, SO_2, CMe

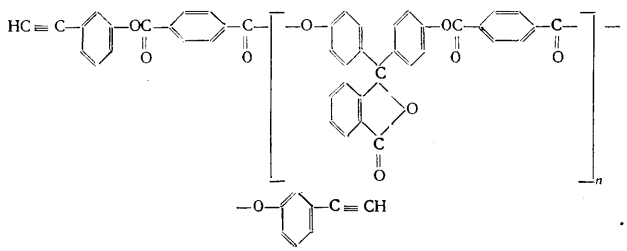
and also hydroquinone and a novolac resin with propargyl bromide in an alkaline medium, oligomers having acetylenic end-groups and capable of thermal polymerisation at 200 °C without the evolution of volatile products were obtained[74].

Oligoesters containing propargyl groups of the following type have been synthesised[75,76]: oligoesterpropargylates



and $(HC{\equiv}CCH_2OCOCH_2CH_2OCO)_2R$, oligocarbonatepropargylates $(HC{\equiv}CCH_2OCO)_2R$, and oligoesterpropiolates $(HC{\equiv}CCOOROCO)_2C_6H_4$ and $(HC{\equiv}CCOOROCO)_2C_2H_4$, where R is a diol residue. It has been shown that they harden at 200–300 °C with formation of cross-linked products and that their thermal stabilities are much higher than those of the analogous polymers with saturated bonds in the chain.

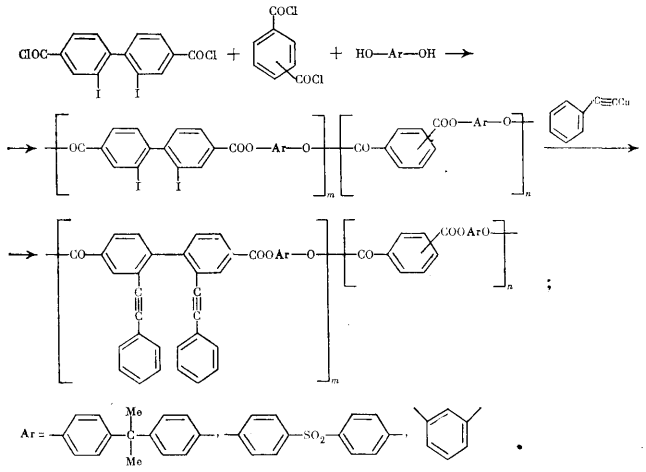
Thermostable thermoreactive aromatic polyesters containing acetylenic groups have been obtained by the polycondensation of aromatic bisphenols (phenolphthalein, phenolphthalimidine, phenolsulphonephthalein, and fluorescein) with the chlorides of isophthalic or terephthalic acid with subsequent addition of ethynylphenol[77]. When phenolphthalein is used together with terephthalic acid chloride and 3-ethynylphenol for the synthesis, the polymer has the following structure:



Glass plastics based on this polyester have a high strength and exhibit low weight losses on thermal ageing (0.4% at 250 °C for 1000 h).

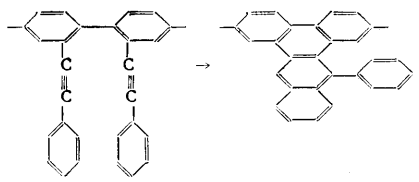
Aromatic polyesters containing phenylethynyl groups have been obtained[78] by the interfacial condensation of the dichloride of 2,2'-di-iodobiphenyl-4,4'-dicarboxylic acid and isophthaloyl or terephthaloyl chloride with bisphenols and subsequent substitution of the iodine by phenylethynyl groups in accordance with the scheme

Scheme 4



The resulting polyesters are soluble in pyridine and tetrachloroethane and harden at 200 °C in argon in the course of 30 h via an intramolecular cyclisation mechanism (Scheme 5):

Scheme 5



Polyesters containing conjugated diacetylenic groups in the chain have been synthesised by the polycondensation of the chlorides of dicarboxylic acids (succinic, azelaic, adipic, sebacic, isophthalic, and terephthalic) with 3,5-hexadiyne-1,6-diol and their photochemical and thermal behaviour has been investigated. The synthesis of epoxide resins containing ethynyl end-groups by the interaction of epoxide oligomers with aminophenylacetylene has been described[80]. The resins were hardened at 250 °C with formation of impact-resistant thermostable polymers.

2. Polyamides

Analogously to aromatic polyesters, aromatic polyamides with phenylethynyl side groups have been obtained by the low-temperature polycondensation of diamines with the dichloride of 2,2'-di-iodobiphenyl-4,4'-dicarboxylic acid or its mixture with the dichloride of biphenyl-4,4'-dicarboxylic acid in dimethylformamide (DMF) followed by the treatment of the iodine-containing polyamides with an excess of copper phenylacetylide[81]. Most of these polyamides were soluble in DMF, had softening temperatures in the range 177–247 °C, and showed weight losses amounting to 1.1–3.9% after three

days at 300 °C. It was established that the solubility of polyamides with an identical structure of the acid component of the molecule decreases in the following sequence of aromatic diamino-fragments:

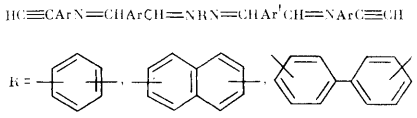


Like polyesters, these polyamides are capable of being hardened via an intramolecular cyclisation mechanism with formation of 9-phenylbenzanthracene units.

Polyamides containing tolane fragments have been obtained by the condensation of the dichlorides of isophthalic and terephthalic acids with 4,4′-diaminotolane in DMF containing LiCl.[82] Polyisophthalamides are soluble in DMF and *N*-methylpyrrolidinone with added LiCl and polyterephthalamides are soluble in sulphuric and methylsulphuric acids. According to thermogravimetric analysis, the temperature of the onset of the thermal decomposition of these polymers is 445–470 °C in air and 490–530 °C in an inert atmosphere.

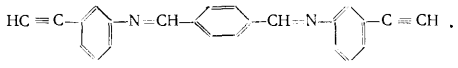
3. Polymeric Schiff Bases

Oligoimines containing acetylenic end-groups and having the following structures can be obtained by the reaction of aromatic aldehydes with aromatic diamines and subsequent treatment of the reaction product with aminoarylacetylene[83]:



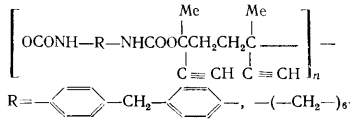
The resulting oligomers are soluble in halogenated solvents. They are capable of hardening on heating. Thus the oligoimine obtained from isophthalic dialdehyde, 1,3-di(3-aminophenoxy)benzene, and 3-aminophenylacetylene has a softening temperature of 40–45 °C and on heating to 150 °C in the absence of air for 16 h it gives rise to a hard material with a glass point T_g = 230–260 °C and remains thermally stable up to 350 °C.

Analogous oligomers have been obtained by the reaction of 3-aminophenylacetylene with terephthalic dialdehyde[84]. In particular, a product having the following structure and a melting point of 136–139 °C has been isolated:

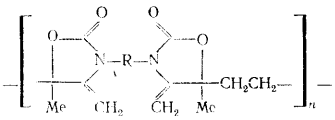


4. Polyurethanes

Acetylene-containing polyurethanes have been obtained by the polycondensation of di(4-isocyanatophenyl)methane and hexamethylene di-isocyanate with 3,6-dimethylocta-1,7-diyne-3,6-diol:[85]



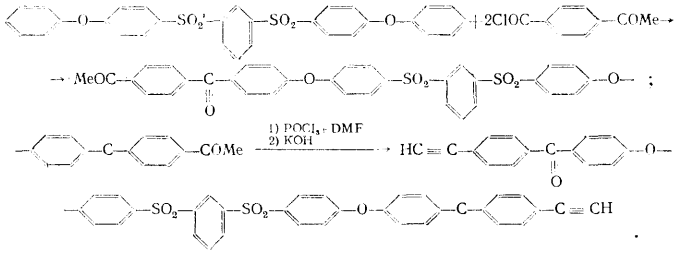
They are soluble in organic solvents and form transparent films. They have a viscosity η_{log} = 0.4–0.54 (30 °C, DMF), T_g = 135° and 54 °C, and temperatures corresponding to a 10% weight loss of 260° and 175 °C respectively. When solutions of the polyurethanes in DMF are heated, intramolecular cyclisation with formation of the corresponding polyoxazolidinones takes place:



The polymers obtained have high glass points T_g = 170–175 °C and a high temperature corresponding to a 10% weight loss (390–410 °C).

5. Polysulphones

Polysulphones with acetylenic end-groups have been obtained by the reaction of 1,3-di(4-phenoxybenzenesulphonyl)benzene with 4-acetylbenzoyl chloride via the following scheme[86]:



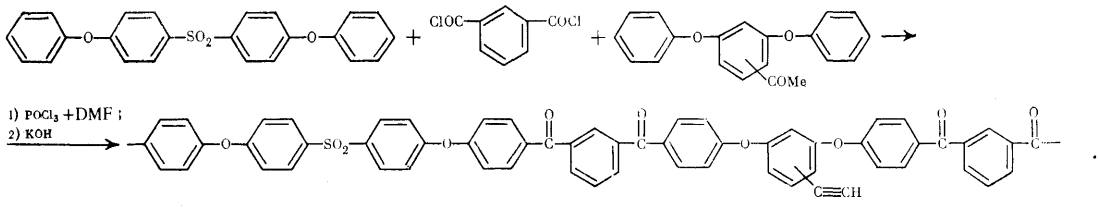
This bisacetylenic oligomer is a relatively low-melting solid soluble in the usual organic solvents: chloroform, dioxane, and tetrahyrofuran (THF). It was hardened in nitrogen at 300 °C. The authors[86] suggest that the hardening proceeds via a polycyclotrimerism with formation of polymers of the type of polyphenylenes. The hardened products have high glass points and a high thermo-oxidative stability. The weight losses at 300 °C in circulating air amounted to 4–6 wt.% after five days.

The question of the synthesis and properties of polysulphones with acetylenic groups has been examined in detail in a review[19]. Here we may mention that the synthesis of a polysulphone with an acetylenic side group via Scheme 6 is possible[87].

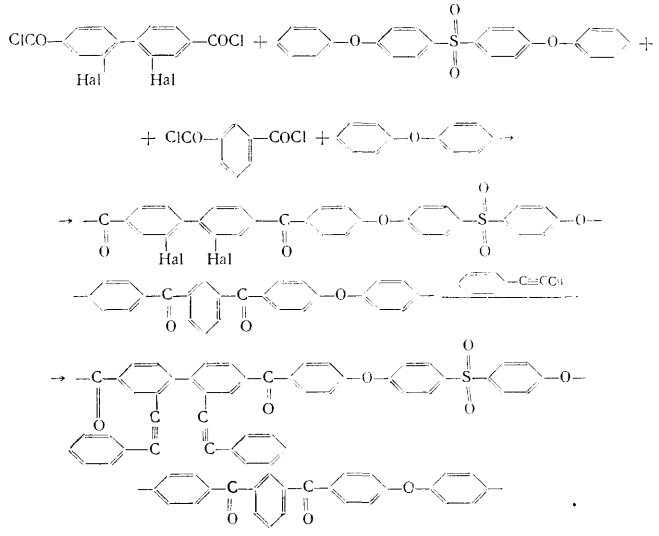
The polymers are soluble in DMF and have η_{log} = 0.23–0.43 and T_{soft} = 185–225 °C. After hardening in the presence of palladium chloride in nitrogen at 210° and 285 °C, they lost their solubility and did not soften up to 300 °C. According to thermogravimetric data, they are thermally stable in an inert atmosphere up to 550 °C and retain their thermo-oxidative stability up to 250 °C.

The sulphone oligomers have also been hardened by the intramolecular cyclisation of derivatives of 2,2′-di(phenylethynyl)biphenyl[88–92]. The oligomers were obtained via Scheme 7:

Scheme 6

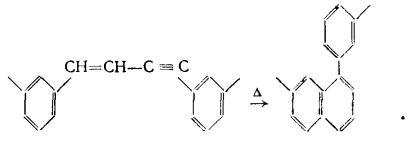


Scheme 7



After the polymers have been hardened in an inert atmosphere at 280 °C for 24 h, their thermo-oxidative stability increases and the weight losses at 300 °C in air amount to 1–2 wt.% (compared with 6–7 wt.% for the unhardened polymer).

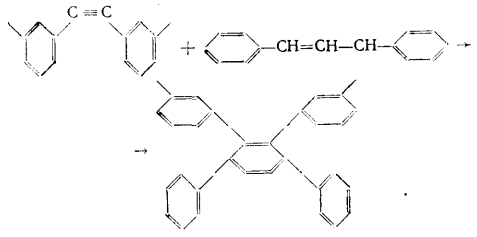
In order to achieve intramolecular cyclisation, polysulphones containing the enyne group in the polymer chain have been synthesised[93–95]:



On heat treatment, the enyne group was converted into the phenylnaphthalene group and the polysulphone was hardened. Such polymers are photosensitive but after hardening they become very brittle.

The Diels–Alder reaction has also been used to harden polysulphones[96]. Polysulphones containing tolane groups were treated with 1,4-diphenylbutadiene in accordance with Scheme 8:

Scheme 8



Among other classes of polymers, mention may be made of acetylene-containing phosphazene copolymers[97] obtained by treating polydichlorophosphazene with propargyl alcohol.

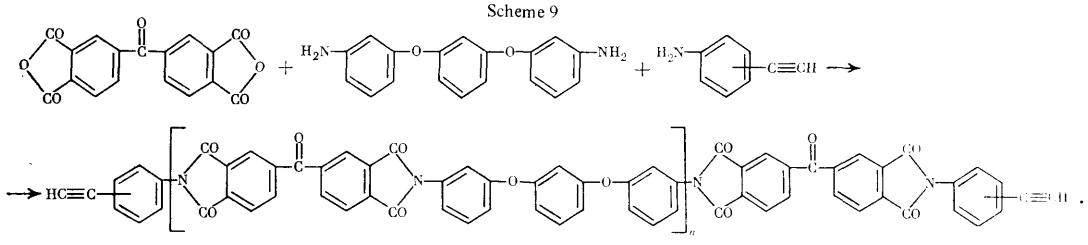
IV. HETEROCYCLIC OLIGOMERS AND POLYMERS

Polyimides, polybenzoxazoles, polyphenyltriazines, and polyphenylquinoxalines have been obtained in the series of heterocyclic polymers containing acetylenic groups.

1. Polyimides

Polyimides with ethynyl end-groups have been described in a number of communications[19,82,98–103]. They are obtained by the condensation of aromatic diamines, for example, 1,3-bis-3-aminophenoxybenzene, with aromatic tetracarboxylic acid dianhydrides, for example, benzophenonetetracarboxylic acid, and of aminophenylacetylenes with the ethynyl-substituted anhydride of an aromatic dicarboxylic acid using a two-stage method in accordance with Scheme 9:

Scheme 9



The thermal and mechanical characteristics of the polyimides have been described[19]. It is noteworthy that the glass points of the hardened polyimides are fairly high (up to 340 °C) and depend on the conditions in the subsequent (final) hardening. Graphite filled plastics with the polyimide binder retain their strength effectively at high temperatures.

Differential scanning calorimetric data[98] have demonstrated the two-stage character of the hardening of the acetylene-containing polyimides. It is believed that the $-C\equiv C-\overset{\overset{\|}{CH_2}}{C}-$ groups are formed initially (at 200 °C), while in the second stage (at 240–260 °C) a third group adds on, which is accompanied by the formation of a benzene ring.

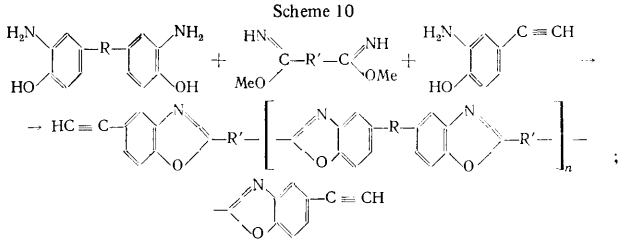
The dialkyl esters of tetracarboxylic acids can be used instead of the dianhydrides for the synthesis of polyimides with acetylenic end-groups[99], while the propargyl ester of aminobenzoic acid can be employed as the ethynyl component[102].

Branched oligoimides containing ethynyl end-groups have been obtained by the reaction of the dianhydride of benzophenonetetracarboxylic acid with aromatic triamines for the introduction of the ethynyl group into the polyimide chain by the reaction of diaminotolane with the dianhydride of pyromellitic acid has been described[82].

2. Polybenzoxazoles

Dibenzoxazole oligomers with fluorocarbon ether linkages and acetylenic end-groups have been synthesised via the Scheme[104]

Scheme 10



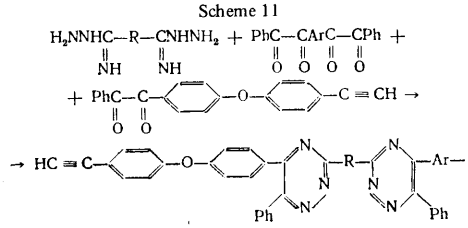
$n = 0, 1, 2$; R=—$CF_2CF_2O(CF_2)_5OCF_2CF_2$—;
R′=—$CF_2(OCF_2CF_2)_xO(CF_2)_3O(CF_2CF_2O)_yCF_2$—; $x + y = 5, 6$.

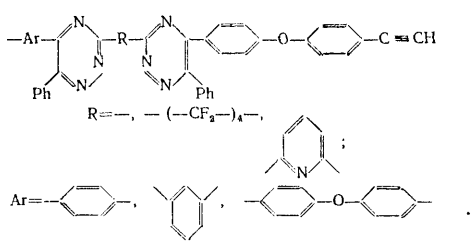
The polymers obtained had glass points ranging from −61° to −56 °C, were hardened via the acetylenic end groups at 180–200 °C, and in the hardened state began to be degraded in air at 375–400 °C.

3. Polyphenyltriazines

Oligophenyl-1,2,4-triazines containing acetylenic end-groups have been obtained by the reactions of bisamidrazones, dibenzils, and 4-(4-ethynylphenoxy)benzil via the scheme[105]

Scheme 11



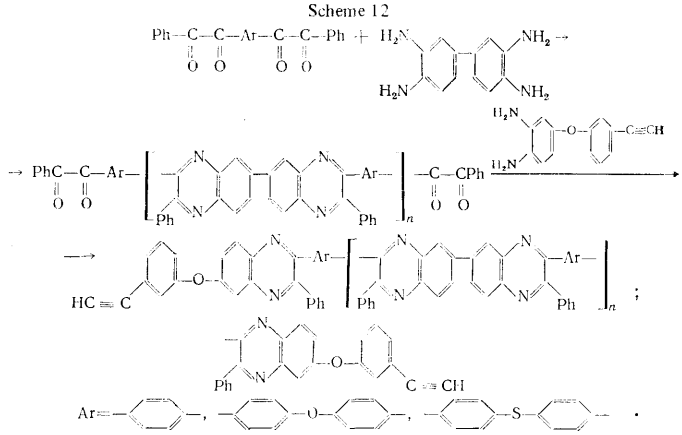


These polymers have a high thermo-oxidative stability and proved promising as binders.

4. Polyphenylquinoxalines

Polyphenylquinoxalines containing ethynyl end-groups have been obtained by a two-stage method in accordance with the scheme

Scheme 12



The scheme shows that oligomers with benzil end-groups were synthesised initially by the reaction of diaminobenzidine with an excess of an aromatic dibenzil and then a solution of 3-(3,4-diaminophenoxy)phenylacetylene was added to the reaction mixture. The polymer dissolves in THF, chloroform, dioxane, and methylene chloride; its cross-linking via the acetylenic end-groups takes place in the temperature range 200–275 °C according to differential scanning calorimetric data; the weight loss begins at 300 °C in air and at 465 °C *in vacuo*.

This and other reactions involving the formation of polyphenylquinoxalines and their properties have been described in detail in a review[9] and here we shall only note some of them. It is possible to synthesise polyphenylquinoxalines containing the 2,2′-(phenylethynyl)biphenylyl groups, which are capable of forming (via intramolecular cyclisation) 9-phenyldibenzanthracene fragments on heat treatment or exposure to radiation[108]. The viscosities of 5% solutions of the polymers obtained in chloroform at 30 °C were $\eta_{log} = 0.18–0.3$, their molecular weights ranged from 15000 to 17200, and their glass points were $T_g = 215–330$ °C. After hardening (at 245–320 °C in nitrogen), the polymers lost their solubility in sulphuric acid, which indicates the occurrence of intermolecular cross-linking.

In order to reduce the T_g of the oligomeric polyphenylquinoxalines with ethynyl end-groups, to increase the fluidity of their melts, and to decrease their hardening time, low-molecular-weight reactive plasticisers were employed:

6-(3-ethynylphenoxy)-3-[4-(3-ethynylphenoxy)phenyl]-2-phenylquinoxaline[109], 1-phenoxy-3-(3-ethynylphenoxy)-benzene, and 1,3-di(3-ethynylphenoxy)benzene[110]. The polyphenylquinoxalines with added plasticiser had T_g = 100 °C, the viscosities of their melts were reduced, and their hardening times and temperatures were lower.

V. THE HARDENING OF THE OLIGOMERS AND PRACTICAL APPLICATIONS OF THE POLYMERS

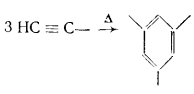
The authors of the present review believe that further progress in the field of the chemistry of polymers with acetylenic linkages will be determined not only by the synthesis of new polymers and the development and expansion of the raw materials resources but also by the development of methods which will ensure a high degree of the reaction involving the triple bond and which will increase the selectivity of the reaction with respect to the formation of aromatic rings in the three-dimensional network on hardening the polymers.

However, at the present time only a low degree of formation of aromatic rings is attained in the hardening of polymers, particularly those with rigid chains which have a high glass point, which is bound to affect their thermo-oxidative stability. Thus it has been established[111] by NMR that the ethynyl groups in polyimides with acetylenic end-groups are converted into aromatic rings to the extent of only 30%, while the remaining groups apparently give rise to olefinic fragments. The mechanisms of the hardening reactions are at present insufficiently clear and Baise[111] has pointed out the possibility of the occurrence of several different reactions of the acetylenic groups during hardening at elevated temperatures. Certain free-radical polymerisation reactions have been described. The pyrolytic cyclotrimerisation of acetylene to benzene or higher aromatic compounds may also proceed with participation of free radicals. There is also a possibility of aromatisation with conversion of acetylene-containing groups into condensed aromatic fragments.

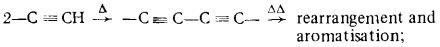
Thus the possibility of the manifestiation of a hetero-unit structure, which is in general characteristic of high-molecular-weight compounds, must be taken into account in processes involving the formation of various fragments during the hardening of compounds with acetylenic linkages[112]. The hetero-unit principle was considered previously in assessing the structures of polyphenylenes in which the main chain structures consisted of mono-, di-, and tri-substituted benzene rings (in different proportions) and also are of residual ethynyl end-groups and possibly defective polyene fragments. By altering the conditions of the synthesis, it was possible to influence within certain limits the structure of the polymer formed. The hardening conditions can also effect the character of the fragments produced.

The problems involved in the hardening of polymers with acetylenic end-groups have been considered[113]. Polymers containing acetylenic end-groups are hardened as a result of the following reactions:

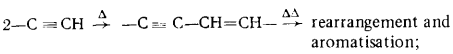
(1) trimerisation[114,115]:



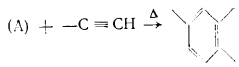
(2) Glaser coupling[116]:



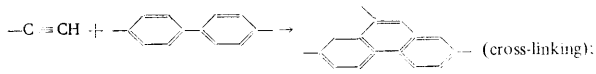
(3) Strauss coupling[117]:



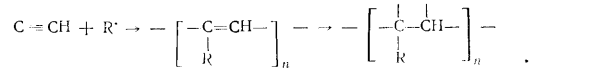
(4) Diels–Alder reaction with participation of the products (A) formed as a result of the Strauss and Glaser coupling[118]:



(5) Diels–Alder reaction in the polymer chain[118]:



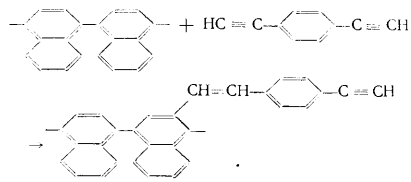
(6) free-radical polymerisation with formation of linear or branched products[118]:



The degree of reaction depends on the hardening of the polymer and on its character (thermal or catalytic)[111], but thermal hardening via the triple bonds is the most convenient method for the conversion of the oligomer into a three-dimensional polymer. Such hardening is usually carried out at 180–250 °C, where the main polymer chain is not degraded; however, it is then necessary to carry out the final hardening at 300–350 °C, since the thermal transformation of the acetylenic groups into aromatic rings takes place at 250–300 °C. This applies to the formation of a thermoreactive binder on the basis of oligophenylenes, developed in the USSR under the brand name "Reaktofen" and in the USA under the brand name "H-Resin".[119]

The oligophenylenes obtained on the basis of diethynylbenzenes are used to prepared articles by sintering, pressing, casting under pressure, and extrusion methods. These plastics can be used for a long time at 315 °C and briefly at 350 °C.[67,104,120] In order to increase the fluidity of the melt and to improve its adhesion to fillers, low-molecular-weight acetylenes are introduced into the resins[105]. Antifriction materials consisting of oligophenylenes, *p*-diethynylbenzene, and antifriction fillers, which are heat-resistant up to 380 °C, have been obtained[121].

The modification of the oligomers by the addition of low-molecular-weight oligomers has found extensive applications. There are patents for ternary and quaternary copolymers containing 25–75% of polyacetylene, obtained by the oxidative dehydropolycondensation of *p*- and *m*-diethynylbenzenes and dipropargyl ethers of phenols, together with 75–25% of low-molecular-weight acetylenes which consist of 1,4-diphenylbutadiyne, 1,3-di(phenylbutadiynyl)benzene, and others[122,123]; the copolymers are used to prepare graphite fibres. Phenol-formaldehyde resins are modified in the same way[124]. Polymers without ethynyl and other reactive groups are hardened using aromatic acetylenes. Thus the oligophenylenes obtained by the oxidative dehydropolycondensation of benzene, naphthalene, and anthracene are hardened with the aid of *p*-diethynylbenzene at 100–280 °C;[125,126] this entails the formation of insoluble and infusible products in almost quantitative yields. The study of the products of the hardening reaction for low degrees of conversion by NMR and infrared spectroscopy and also the investigation of the molecular weight distribution led to the following hardening mechanism:



Polyphenylenes can be used in the form of compositions for the construction of rocket nozzles, as ablation materials, and in composite materials together with carbon fibres for the construction of turbine blades and other devices which can operate for a long time at high temperatures and possess high resistance to wear. As a consequence of the satisfactory electrical, physical, and chemical characteristics, these polymers are promising for the preparation of electrical insulators, protective coatings, lining materials and filters in the form of compositions with metals, asbestos, and glass and carbon fibres, all components capable of being used at high temperatures[65].

The likely usefulness of polyimides with acetylenic groups as binders for carbon and glass plastics has been demonstrated[98,99]. Polyphenylquinoxalines are suitable for the preparation of adhesion materials[127] and polysulphones are capable of forming films which retain strength and flexibility after hardening[92]. Polymeric Schiff bases[83] serve as effective varnish coatings and impregnating materials and can be used to prepare semiconducting and conducting materials.

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The problems containing the employment of acetylenic compounds in the synthesis and chemical modification of polymers examined in this review are at present extremely urgent and offer much promise from the standpoint of both the preparation on their basis of traditional polymers with more effective operating characteristics and for the preparation of materials with fundamentally new properties.

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Nesmeyanov Institute of
Organoelemental Compounds,
USSR Academy of Sciences,
Moscow

Russian Chemical Reviews

April 1984

Translated from *Uspekhi Khimii*, 53, 545-565 (1984)

U.D.C. 661.185.1+547.96+541.128.135+542.98

A Microheterogeneous Medium for Chemical (Enzymic) Reactions Based on a Colloidal Solution of Water in an Organic Solvent

Yu.L.Khmel'nitskii, A.V.Levashov, N.L.Klyachko, and K.Martinek

The structure and properties of inverted surfactant micelles in non-polar solvents are examined. The methods for the solubilisation of proteins (enzymes) in such systems and the molecular mechanisms of solubilisation are characterised. The kinetics of chemical enzymic reactions in inverted micelle systems are discussed. The factors influencing the catalytic activity and substrate specificity of the solubilised enzymes are analysed. The characteristic features of the shift of the chemical equilibrium in inverted micelle systems are considered and the prospects for the employment of such systems in fundamental research (particularly in the modelling of the structure and functions of biological membranes) and for the solution of applied problems in chemistry are discussed.
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I. INTRODUCTION

The most important elements in a chemical process are the selection of the reaction medium and the catalyst. Enzymes are the best catalysts of chemical reactions available at present. Their exceptionally high catalytic activity under mild conditions and the unsurpassed selectivity of their action[1] lead to extensive prospects for the employment of biocatalysis in technological processes[2]. The use of enzymes as catalysts in fine organic synthesis and in the preparation of medicinal drugs and valuable biologically active compounds is particularly promising. However, the wide scale employment of enzymes in practice is hindered by the fact they retain their unique catalytic properties usually only in

aqueous solution. On the other hand, it is known that many chemical reactions are driven by thermodynamic factors towards the required product only in specific organic solvents. This is associated both with specific solvation effects and with the solubilities of the individual reaction components or, in other cases, with the fact that water is formed together with the required product and the equilibrium is therefore displaced towards the starting materials when the reaction is carried out in aqueous solutions. Unfortunately the transition from water as the reaction medium to an organic solvent entails as a rule either complete denaturation of the enzyme or a sharp decrease of its catalytic activity and the disappearance of its substrate specificity[3].

One of the possible ways out of this situation is the creation of model catalytic systems, soluble in organic solvents, which make it possible to approach to some extent the efficiency of catalysis by enzymes in aqueous solutions. In particular, systems of inverted surfactant micelles in organic solvents can be used as such model systems. The inverted micelles consist of closed aggregates of associated surfactant molecules whose outer layer is made up of their hydrocarbon fragments and whose nucleus consists of their polar (ionic) groups. Such associated species are capable of solubilising in organic solvents considerable amounts of polar compounds, which are located within the inner cavity (nucleus) of the micelle.

The unique properties of the micromedium in the inner cavity of inverted micelles, namely a reduced polarity, a high microviscosity, and a high concentration of functional groups, justify the consideration of the inner cavity of inverted micelles as an extremely realistic model of the micromedium in the active centres of enzymes[4,5]. Indeed many reactions are greatly accelerated when they are carried out in systems of inverted micelles and the acceleration effects sometimes approach in order of magnitude those observed in enzyme catalysis[6]. The acceleration of reactions in inverted micelle systems is caused, apart from the trivial effect arising because the reactants are concentrated as a result of being bound to the micelles and the effects of the micromedium in the inner cavity, by the rigid fixation of the reactant molecules to the inner cavity of the micelles[6,7] as happens in enzyme catalysis[1]. Effects associated with specificity in relation to the size[8] and configuration[9] of the reactant molecules, characteristic of enzyme catalysis, can also be observed in catalysis by inverted micelles.

It is noteworthy that the acceleration and specificity effects, comparable in magnitude to those observed in enzyme catalysis, are manifested in an inverted micelle system only in individual instances and are not general. A procedure, which would permit a direct combination of the advantages of an enzyme as a catalyst with the advantages of an organic solvent as the reaction medium is therefore more promising. Its fundamental idea is to "force" enzymes to operate in an organic solvent with a low water content. Evidently, in employing this approach, it is necessary to solve the problem of the stabilisation of the enzyme in relation to the denaturing effect of the organic solvent[3].

This problem can be solved in principle by employing as the reaction medium a "water–water-immiscible organic solvent" system or an organic solvent which ensures the integrity of the native structure of the enzyme globule and hence its catalytic activity[10]. Another solution of the problem has been found recently. Namely we have shown[11], and this was subsequently confirmed in studies by other investigators (which are discussed below), that water-soluble enzymes can be solubilised in organic solvents with the aid of surfactants and that their catalytic activity can be simultaneously preserved. As a result of the solubilisation, the enzyme is incorporated in the inner cavity of an inverted surfactant micelle, as shown in Fig.1, and is thereby protected from the denaturing action of the organic solvent.

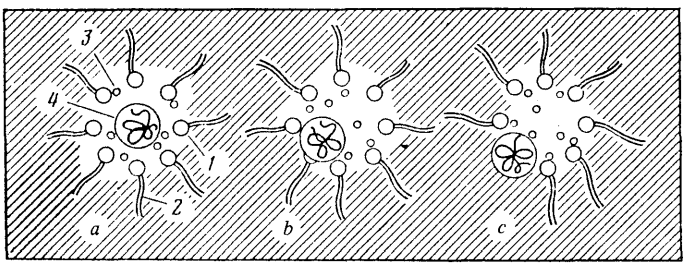


Figure 1. Schematic representation of an inverted micelle containing hydrophilic (*a*), surface-active (*b*), and hydrophobic (*c*) proteins: *1*) ionic (polar) group in the surfactant molecule; *2*) hydrocarbon group in the surfactant molecule; *3*) counterions and/or solubilised water molecules; *4*) enzyme molecule; the organic solvent is shown shaded.

We shall consider the principal aspects and achievements in this new field—micellar enzymology, which permits the employment of biocatalysts for the acceleration of chemical reactions in an organic solvent.

II. PHYSICOCHEMICAL PROPERTIES OF INVERTED MICELLES

The Structure of Inverted Micelles

In non-polar organic solvents inverted micelles consist of associated surfactant species whose inner component is made up of the polar "heads" and whose outer layer consists of the hydrocarbon "tails" of these molecules. The micelle-formation process in a non-polar medium can be described[12] in some cases within the framework of the mass action model, which presupposes an equilibrium between the monomeric surfactant molecules and the micelles of the "all or nothing" type and in other cases by a stepwise model, according to which a set of associated species with different aggregation numbers, which are in equilibrium with one another, exist in solution.

The size and form of the inverted micelles are closely related to the micelle formation mechanism: in the case of the mass action mechanism the micelles are nearly spherical, while in the case of the stepwise mechanism they assume extended, rod-like and lamellar structures[13]. The linear dimensions of the micelles do not usually exceed several tens of Angstroms. The micelles formed via the mass action mechanism are usually characterised by a narrow distribution with respect to size and shape, which is independent of the surfactant concentration[14–16]; this feature applies mainly to systems with anionic surfactants. In the case of surfactants undergoing association via the stepwise mechanism (these are as a rule cationic surfactants) the micelles are polydisperse and the distribution shifts towards larger associated species as the surfactant concentration rises[13,17,18].

On solubilisation of water in surfactant solutions in non-polar solvents, hydrated micelles are formed and differ significantly in their size and shape from the micelles which

exist in anhydrous systems. The hydration of the micelles reduces the degree of their asymmetry, since they acquire an almost spherical shape[19,20], and leads to a sharp increase of their size and molecular weight owing to the formation of a water-filled microcavity within the inverted micelle[16,19-23]. For example, in the system of inverted micelles formed by the sodium salt of the di-iso-octyl ester of sulphosuccinic acid (OT or AOT aerosol) in iso-octane, an increase of the degree of hydration, i.e. of the molar ratio $[H_2O]/[AOT]$, from 0 to 50 entails an increase of the hydrodynamic radius of the micelle from 17 to 120 Å.[22]

The Micromedium in the Inner Cavities of Inverted Micelles

The water filling the inner cavities of the hydrated inverted micelles differs in its physicochemical properties from the usual (bulk phase) water. The scale of the differences is determined by the degree of hydration by the inverted micelles, which is usually expressed as the ratio of the molar concentrations $[H_2O]/[\text{surfactant}] = w_0$. For low values of w_0 (of the order of several units), the properties of the micellar and bulk-phase water differ greatly but, as w_0 increases, the differences are gradually smoothed out. The cause of this is that the first portions of the water added to the system are bound firmly to the surfactant molecules as a result of the hydration of their polar components. The amount of strongly bound water is 4–10 molecules per surfactant molecule depending on the nature of the latter. The so-called "free" water, constituting an independent microphase and approaching in its properties the bulk-phase water, appears within the inverted micelles only after the completion of the hydration of the surfactant[20,24,25]. For example, for low values of w_0, the viscosity of the water solubilised by the inverted AOT micelles in an aliphatic hydrocarbon exceeds that of the bulk-phase water by a factor greater than 200 and its polarity corresponds to that of chloroform; with increase of w_0, these differences between the properties of the micellar and bulk-phase water decrease monotonically and disappear[25,26].

The aqueous cavities of the hydrated inverted micelles are inhomogeneous in their physicochemical properties and are characterised by different local polarities, viscosities, etc. at different points[20,26,27]. For example, the local viscosities and polarities of water within the cavities of the hydrated inverted AOT micelles in iso-octane respectively decrease and increase on moving away from the boundary of the aqueous cavity to its centre[26]. The existence of the inhomogeneity can be explained by the presence within the micelle of layers of water of hydration bound to different extents[20,26,27].

The pH Values in the Inner Cavities of the Inverted Micelles

The inner cavity of a hydrated inverted micelle is characterised by a high concentration of electric charges arising on ionisation of the polar groups in the surfactant molecules. As a result of this, the local pH of the aqueous cavity can differ significantly from the pH of the solubilised aqueous solution[28-32]. The question of the pH assumes a particular importance in the study of chemical (and particularly enzymic) reactions in the inner cavities of the inverted micelles.

In order to estimate the acid–base properties of the micromedium in the inner cavities of the inverted micelles, the method based on comparing the pK_a of different indicators dissolved in pure water and solubilised by the inverted micelles is most widely employed[29-32]. Analysis of the data obtained with the aid of the indicator method permits the conclusion that the micromedium in the inner cavity is in general more acidic than the initial aqueous solution in the case of an anionic surfactant[29,30] and more alkaline in the case of a cationic surfactant[32]. The pH shift is ~1–2 units. When a non-ionic surfactant is employed, the acidity in the inner cavity of the micelles hardly differs from that in the initial aqueous solution[31].

A new approach to the determination of the pH in the inner cavities of the inverted micelles, in which the dependence of the chemical shift of the ^{31}P NMR signal due to the ^{31}P nucleus, forming part of the composition of the phosphate ion, on the pH of the surrounding medium employed is used, has been proposed recently[28,33]. A relation between the pH of the aqueous cavity in an inverted AOT micelle in iso-octane and the initial aqueous solution (the "acidity scale") has been obtained with the aid of this method[28]. The pH shifts determined in this way agree with the values obtained by the indicator method[29,30].

Both approaches described suffer, however, from significant disadvantages. In particular the pK_a of the solubilised "reporter" molecule (indicator or phosphate anion) cannot be determined independently, which necessitates appropriate assumptions and hence leads to an uncertainty in the pH value obtained.

The Reactivity of the Water Solubilised by Inverted Micelles

The rates of chemical reactions involving water as a rule increase sharply on passing from an aqueous solution to a system of hydrated inverted micelles and the acceleration effect can reach a factor of 10^6 and more[5,34,35]. The acceleration effect is largely due to the high reactivity of the water solubilised in the inner cavities of the inverted micelles where the reaction takes place. For example, the nucleophilic activity of the water solubilised by inverted AOT micelles is at least 10^3 times higher than that of the bulk-phase water[5,35]. The water which is either involved in the hydration of the polar groups in the surfactant molecule[5,36] or appears directly after the completion of the hydration[35] shows the highest reactivity. Further addition of water leads to the formation of hydrogen bonds between the water molecules themselves which results in a decrease of their reactivity[36]. The high reactivity of the water molecules involved in the initial hydration of the surfactant can be caused by the high mobility and/or the change in their acid–base characteristics[5].

III. METHODS FOR THE INCORPORATION OF THE PROTEIN (ENZYMES) IN INVERTED MICELLES

Homogeneous (optically transparent) solutions of proteins (enzymes) in organic solvents can be obtained by employing one of the following three procedures.

The first procedure was proposed by ourselves[11] and is nowadays most widely used[37-44]. A small amount (of the order of several volume per cent) of the aqueous protein solution was introduced into a surfactant solution in an organic solvent (the actual ratio of the volumes of the aqueous and organic solutions is determined by the object of the experiment, the required degree of hydration of the surfactant, etc.). The resulting mixture is vigorously shaken (for several tens of seconds) until the formation of an optically transparent solution. Exposure of the

mixture to ultrasound is also used instead of mechanical shaking[45,46]. It must be emphasised that the choice of the method of stirring is important in the study of enzymes and particularly enzyme kinetics in inverted micelle systems, because the time taken to attain equilibrium in the colloidal system depends on its efficiency: in some cases the equilibration time in inverted micelle systems (in the absence of a solubilised protein) can be measured in hours and tens of hours (see, for example, Becher and Clifton[47] and Corkill et al.[48]).

The equilibration time in surfactant solutions apparently depends to a considerable extent on the nature of the surfactant and/or solvent. For solutions of one of the most widely used surfactants—the OT (OAT) aerosol—in aliphatic hydrocarbons, it has been shown[22,49] that equilibrium (the attainment of constant dimensions of the micelles) is established rapidly and there is no need for ultrasonic treatment. We arrived at an analogous conclusion using the same surfactant for the solubilisation of enzymes[50]. The question of the necessity for the ultrasonic treatment can, however, arise when other surfactants are used. One must then bear in mind that the action of ultrasound can inactivate the enzyme[51]. In the solubilisation of aqueous enzyme solutions without the application of ultrasound, there is virtually no inactivation of the enzyme[11,41,52,53].

The second procedure, proposed in Menger's laboratory[54], consists in the initial introduction of the required amount of water into the surfactant solution in an organic solvent (in order to attain the required degree of hydration of the surfactant), after which a dry (lyophilised) protein is dissolved in the resulting transparent solution with vigorous shaking. The time required for the dissolution of the dry protein is usually greater than in the procedure employing aqueous solutions but it diminishes with increase of the degree of hydration of the surfactant[50]. The complete dissolution of the dry protein sample takes place only at moderate protein concentrations, comparable to those obtained by the first method[50].

In order to obtain highly concentrated protein solutions, an excess of the dry protein is introduced into the surfactant solution in an organic solvent and its undissolved part (after several hours) is separated by centrifugation[50]. The repetition of the procedure for the dissolution of the protein in the resulting supernatant increases the protein content in the micellar solution. When this method is used to obtain concentrated protein solutions, it is necessary to monitor the surfactant and water contents in the supernatant after separating the soluble component, because the latter can entrain both the surfactant and water.

The third solubilisation method, proposed by Luisi and co-workers[55,56], involves the spontaneous transfer of the protein in a two-phase system consisting of approximately equal volumes of the aqueous protein solution and the organic solvent containing the surfactant. After the completion of the solubilisation, carried out with slight stirring or altogether without stirring, the organic phase containing the dissolved protein is separated. A disadvantage of this method is the long time required for the solubilisation process. In addition, the problem of determining the amount of water solubilised by the micelles (the degree of hydration of the surfactant) arises.

We draw attention to the fact that, for very low values of $w_0 < 1-2$, proteins are almost insoluble in inverted micelle systems. The solubilisation of the protein begins only for a certain value of w_0, beyond which an increase of the degree of hydration of the surfactant is accompanied by an almost linear increase of the solubility of the protein up to concentrations comparable to those attainable in an aqueous solution[50]. The specific solubilisation limits depend on the temperature, the pH of the aqueous solution, the nature of the surfactant, the concentrations of water and the surfactant in the system, and also the nature of the protein[41,50].

Molecular Mechanisms of the Incorporation of the Protein in Inverted Micelles

In organic solvents inverted micelles provide a methodologically unique possibility for the dissolution of proteins of different kinds under standard conditions where the dissolved protein molecule can itself "select" the microenvironment corresponding to its nature (optimal from the thermodynamic standpoint). In fact, as can be seen from the schematic illustration in Fig. 1*a*, the molecule of a hydrophilic protein can avoid direct contact both with the organic solvent and with the surface of the inner cavity of the inverted micelle formed by the polar "heads" of surfactants molecules, being localised in the aqueous nucleus of the hydrated inverted micelle. Surface-active enzymes, for example lipases, are able to interact with the surface layer of the inverted micelle or can be even partly immersed in the latter (Fig. 1*b*). Finally, typical membrane enzymes, can, in principle, come into contact even with an organic solvent, provided that this is favoured by thermodynamic factors (Fig. 1*c*).

Examples of the solubilisation by inverted micelles of enzymes of different kinds, corresponding to type *a*,[11,37-45,52-59] *b*,[60,61] and *c*,[46,62] have been described in the literature (Fig. 1). In all cases the solubilisation results in the formation of an optically transparent solution and the solubilised enzymes retain their catalytic activity. Only the molecular mechanism of the solubilisation of proteins (enzymes) of type *a* (Fig. 1), i.e. the water-soluble proteins, has been investigated quantitatively[38,63,64]. In particular, it has been shown by sedimentation analysis[63,64] that the molecules of typical water-soluble proteins (lysozyme, trypsin, α-chymotrypsin, ovalbumin, alcohol dehydrogenase, and γ-globulin) are capable of being incorporated into inverted AOT micelles in octane over a wide range of experimental conditions without a significant change in the initial dimensions of the micelle. This result agrees with the scheme in Fig. 1*a* and indicates the absence of a significant interaction of the protein with the surfactant.

IV. KINETIC THEORY OF CHEMICAL REACTIONS IN INVERTED MICELLE SYSTEMS

The rates of many chemical reactions increase sharply when they are transferred from an aqueous medium or an organic solvent to organic solvent–surfactant or organic solvent–surfactant–water systems (see the relevant reviews[6,24,65]). In discussing the reaction acceleration effects, the term "micellar catalysis" (which has come to be generally accepted for aqueous systems) must, however, be used with caution because the increase of the rates of reactions in the presence of surfactants in organic solvents is by no means always caused by micellar effects[66]. In certain cases inverted micelles are not formed at all and the acceleration can be achieved as a result of the homogeneous-catalytic effect of monomeric surfactant molecules[66].

Analysis of the numerous experimental data available at present permits the conclusion that in those cases where the acceleration is indeed micellar in nature, it can be caused by

the operation of factors analogous to those which ensure[67,68] the increase of the rates of reactions in aqueous micellar systems. Namely the acceleration can be due to the reactants becoming concentrated as a result of their binding to the micelles, the catalytic action of the polar groups in the surfactant molecules, the rigid fixation and/or orientation of the reactant molecules in the inner cavity of the micelles, and also the characteristic features of the micromedium in the inner cavity where the reaction takes place (reduced dielectric constant, increased reactivity of water, and a shift of the pK_a of the ionic groups of the interacting molecules).

In the kinetic analysis of chemical reactions in an inverted micelle system, it is necessary in the first place to take into account the distribution of the reactants in this microheterogeneous medium. The analogous problem in micellar catalysis in aqueous solutions has already been adequately solved[67,68] within the framework of the pseudophase model. The pseudophase approach can also be employed in the study of the kinetics of chemical reactions in inverted micelle systems.

According to the pseudophase model[69], a surfactant solution consists of the bulk phase of the organic solvent and the micellar "phase" and there is an equilibrium distribution of the reactants between these phases, for example:

$$A_{bulk} \overset{P_A}{\rightleftharpoons} A_{mic}, \qquad (1)$$

where P_A is the partition coefficient of the reactant A:

$$P_A = [A]_{mic}/[A]_{bulk}. \qquad (2)$$

Here and henceforth the subscripts "mic" and "bulk" refer respectively to the micellar and bulk phases. The concept of the set of micelles as an independent "continuous" phase agrees with experimental data, which indicate the free character of the intermicellar exchange of the solubilised molecules[45,70-74]. The applicability of the pseudophase model is limited by the assumption that the equilibrium distribution of the reactants between the phases [formula (1)] does not shift as a consequence of the chemical reaction, i.e. the exchange of matter between the phases is fairly rapid (takes place at diffusional rates). This assumption, which is valid for normal surfactant micelles in aqueous solutions[68], remains in force also on passing to inverted micelle systems[75-78]. We shall consider the application of the pseudophase approach to the analysis of chemical reactions of various types occurring in inverted micelle systems.

First-Order Reactions

Within the framework of the pseudophase model, first-order reactions can be described by the following scheme:

$$\begin{array}{ccc} A_{bulk} & \overset{P_A}{\rightleftharpoons} & A_{mic} \\ \downarrow k_{bulk} & & \downarrow k_{mic} \\ \text{products} & & \text{products} \end{array} \qquad (3)$$

where k_{bulk} and k_{mic} are the true rate constants for the transformation of A in the bulk phase and micellar phase respectively and the partition coefficient P_A is specified by Eqn.(2). Under conditions where [surfactant] $\gg$ [A], the expression for the effective rate constant is[67,68]

$$k_{obs} = (k_{bulk} + k_{mic}P_A cV)/(1 + P_A c) \qquad (4)$$

where c is the concentration obtained after subtracting the critical concentration for micelle formation (CCM), V the molar volume of the surfactant, and $cV \ll 1$ the volume fraction of the micellar phase. It follows from Eqn.(4) that the dependence of k_{obs} on c has the form of a curve with a plateau, which is indeed observed experimentally[4,5,79-81]. The limiting value of k_{obs} is equal to k_{mic} and characterises the true reactivity of the reactant A in the micellar medium.

Second-Order Reactions

Kinetic analysis of a second-order reaction $A + B \xrightarrow{k_{obs}}$ products, occurring in a micellar system under the conditions of strong binding of the reactants to the micelles, leads to the following expression for the dependence of the observed reaction rate constant on the surfactant concentration[67,68]:

$$k_{obs} = \frac{(k_{mic}/V)\,K_A K_B c + k_{bulk}}{(1 + K_A c)\,(1 + K_B c)} \qquad (5)$$

where $K_A = P_A - 1$, $K_B = P_B - 1$, and $P_A \gg 1$ and $P_B \gg 1$ are the partition coefficients of the reactants A and B between the phases determined in accordance with Eqn.(2). According to Eqn.(5), the dependence of k_{obs} on c should be represented by a curve with a maximum, which agrees with experimental data[82,83]. The proposed methods for the linearisation of the experimental k_{obs}–c curves[67,68] make it possible to find both the true rate constants k_{mic} in the micellar medium and the binding constants.

As a general comment on Eqns.(4) and (5), one must emphasise that, in the study of the dependence of k_{obs} on c within the framework of the model discussed, the surfactant concentration should be varied in such a way that the ratio $[H_2O]/[\text{surfactant}]$ is kept constant. In other words, the change in the surfactant concentration should be always accompanied by the corresponding change in the water concentration and conversely. Otherwise a change in c leads to an alteration of the properties of the micromedium within the inner cavities of the inverted micelles where the reaction proceeds (see Section II) and hence to a change in k_{mic} and a distortion of the type of dependence of k_{obs} on c predicted by Eqns.(4) and (5).

Enzymic Reactions in Inverted Micelle Systems

We shall consider the kinetics of the reaction between the enzyme E and the substrate S proceeding in accordance with the Michaelis mechanism

$$E + S \rightleftharpoons ES \rightarrow E + \text{products} \qquad (6)$$

in an organic solvent–water–surfactant system. We shall assume that an equilibrium distribution of the substrate between the phases has been established:

$$S_{bulk} \overset{P_S}{\rightleftharpoons} S_{mic}, \qquad (7)$$

where P_S is the partition coefficient of the substrate:

$$P_S = [S]_{mic}/[S]_{bulk}. \qquad (8)$$

The distribution of the enzyme need not be considered because proteins are almost insoluble in hydrophobic solvents[84]; in addition, enzymes are as a rule denatured in non-aqueous media (see the review of Martinek and Berezin[85]). We shall therefore assume that the catalytic activity is concentrated only in the micellar phase.

The rate of reaction (6) in the micelles, referred to the bulk phase of the entire system, can be expressed (in the initial instant when the concentration of the products is low compared with the initial concentration of the substrate,

in the presence of an excess of the substrate relative to the enzyme, and under stationary conditions) in the form of the Michaelis–Menten equation:

$$v = \frac{k_{cat,mic}[E]_{0,mic}[S]_{0,mic}}{K_{M,mic} + [S]_{0,mic}} \cdot \theta \qquad (9)$$

where θ is the volume fraction of the micellar phase and the subscript 0 indicates initial concentrations.

We shall assume that the exchange of substrate molecules between the phases is fairly rapid, i.e. the occurrence of the enzyme reaction (6) does not impair equilibrium (7). The concentrations of the reactants can then be found from Eqn.(8) and the material balance equations:

$$[S]_{0,mic} = [S]_{0,mic}\theta + [S]_{0,bulk}(1-\theta)$$
$$[E]_{0,tot} = [E]_{0,mic}\theta \,. \qquad (10)$$

However, one should remember that Eqn.(8) is valid only for fairly dilute solutions and the reactant concentrations must therefore be much lower than the surfactant concentration.

After substituting Eqns.(8) and (10) in Eqn.(9), we have

$$v = \frac{k_{cat,app}[E]_{0,tot}[S]_{0,tot}}{K_{M,app} + [S]_{0,tot}} \qquad (11)$$

where

$$k_{cat,app} = k_{cat,mic} \qquad (12)$$

$$K_{M,app} = K_{M,mic}[1+\theta(P_S-1)]/P_S \,. \qquad (13)$$

In the case of a reaction involving a charged substrate, Eqn.(13) can be simplified by assuming that the substrate molecules exist only in the aqueous micellar phase and hence not only $P_S \gg 1$ but also $P_S\theta \gg 1$. Then

$$K_{M,app} = K_{M,mic}\theta \qquad (14)$$

Here we have considered only the simplest pseudophase model[52,86,87], which presupposes a uniform distribution of the reactants throughout the bulk of the hydrated micelles. In the general case the model must naturally be more complex and must take into account the microheterogeneity of the inner cavities of the inverted micelles; in particular, one could take into account the distribution of the substrate between the inner surface layer and the aqueous nucleus of the inverted micelle. Nevertheless, even the simplest model and the equations obtained within its framework permit a successful kinetic analysis of enzymic reactions in inverted micelle systems.

In order to determine the "true" parameters of the Michaelis equation, characterising the enzymic reaction in the aqueous micellar phase, it is necessary to investigate the dependence of the observed rate of the enzymic reaction on the ratio of the bulk phase (organic solvent) and the aqueous micellar phase. The volume fraction of the aqueous micellar phase θ should then be varied in such a way that the ratio w_0 is kept constant, i.e. the properties of the aqueous micellar phase itself are not altered (see Section II).

The validity of Eqns.(11)–(14) has been confirmed[52,86,87] in relation to the trypsin-catalysed hydrolysis of the *p*-nitroanilide of *N*-benzoyl-D,L-arginine in the system of the inverted micelles of cetyltrimethylammonium bromide in a 1:1 chloroform–octane mixture. The dependence of the observed kinetic parameters of this reaction ($K_{M,app}$ and $k_{cat,app}$) on the volume fraction of water in the system is illustrated in Fig.2. Evidently conditions can be achieved (for low values of θ) where, according to Eqn.(14), the observed $K_{M,app}$ is superior to (smaller than) K_M in an aqueous solution (indicated by the dashed line in Fig.2). In principle, by virtue of this factor, it is possible to achieve higher observed reaction rates in an inverted micelle system than in an aqueous solution.

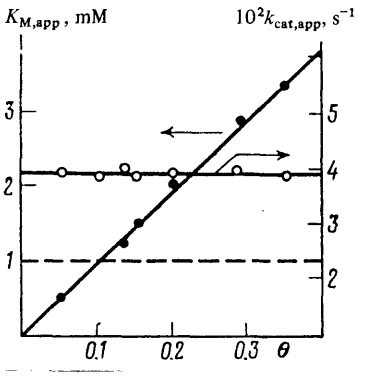


Figure 2. Hydrolysis of the *p*-nitroanilide of *N*-benzoyl-D,L-arginine catalysed by trypsin solubilised in the system cetyltrimethylammonium bromide–aqueous buffer (0.02 M phosphate–borate–acetate, pH 8.0)–1:1 chloroform–octane mixture[86]. The Michaelis parameters $K_{M,app}$ and $k_{cat,app}$ are plotted as a function of the volume fraction of water θ in the system with $[H_2O]/[surfactant] = 25$ and [surfactant] = 0.1–0.8 M. Experimental conditions: 26 °C, $[E]_{0,tot} = 5 \times 10^{-6}$ M. $K_{M,app}$ for the reaction in water is indicated by a dashed line.

This phenomenon, which has long been known for organic (non-enzymic) reactions in micellar solutions[67,68], is associated with the fact that the reactants become concentrated in the micelle. In principle, the concentration effect influences all the kinetic parameters whose dimensions include concentration. On the other hand, Fig.2 shows that the quantity K_{cat}, which has the dimensions [time^{-1}], is independent of θ and hence the observed value of k_{cat} is equal to the true value of this constant for the reaction in the aqueous micellar phase [see Eqn.(12)]. This is precisely why the *true* reactivity of the enzyme and hence its state in the micelle can be inferred from the observed value of $k_{cat,app}$.

V. CATALYTIC ACTIVITY OF SOLUBILISED ENZYMES

The Influence of the Degree of Hydration of the Inverted Micelles

One of the most striking effects observed in the study of enzymes in inverted micelle systems is the dependence of the catalytic activity of the solubilised enzymes on the degree of hydration of the inverted micelle w_0, i.e. on the parameter which determines the size and properties of the micromedium within the inner cavities of the micelles. The dependence of the catalytic activity on w_0 has been observed for enzymes such as α-chymotrypsin[40,52,58,87], trypsin[88], lysozyme[41], phospholipase A_2,[60] alcohol dehydrogenase[52], pyrophosphatase[52,57,87], and pancreatic lipase[61]. As a rule, this dependence is bell-shaped, i.e. there is an optimum value of w_0 for which the catalytic

activity of the solubilised enzyme is a maximum. The optimum values of w_0 differ for different enzymes.

As an example, we shall consider the dependence of the rate constant k_{cat} for the deacylation of *N*-trans-cinnamoyl-α-chymotrypsin, solubilised by inverted AOT micelles in octane, on the degree of hydration, which is illustrated in Fig.3. The possible causes of the appearance of the maximum in the relation between k_{cat} and w_0 have been analysed in detail[58]. Here we shall draw attention to the fact that, under the conditions of the maximum, k_{cat} exceeds the value observed in an aqueous solution (shown by a dashed line in Fig.3). This phenomenon of the "superactivity" of the α-chymotrypsin solubilised by inverted AOT micelles has also been observed by other workers[40,54]. The phenomenon of superactivity is apparently partly due to the effects of the microenvironment of the enzyme molecule in the inverted micelle.

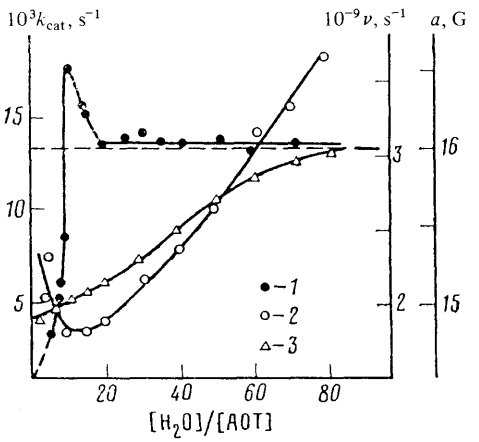


Figure 3. Dependence of the first-order rate constant k_{cat} for the deacylation of *N-trans*-cinnamoyl-α-chymotrypsin (curve *1*), the rotational frequency ν (curve *2*), and the hyperfine splitting constant *a* (curve *3*) for the spin-labelled α-chymotrypsin on the ratio $[H_2O]/[AOT]$ in the AOT (0.1 M)–octane–water (0.05 M tris buffer, pH 8.0) system at 25 °C.[89] The 4-iodoacetamido-2,2,5,5-tetramethylpyrrolidin-1-ylo y-radical was used as the spin label. The values of k_{cat} and *a* in aqueous solution are indicated by the dashed line.

Indeed, Fig.3 shows that the enzyme exhibits the maximum activity for moderate degrees of hydration of the surfactant, i.e. under conditions where the microenvironment of the enzyme molecule within the micelle differs significantly from that in aqueous solution. In particular, it follows from Fig.3 that the hyperfine splitting constant *a* of the EPR signal of a spin label introduced into the active centre of α-chymotrypsin is smaller under the conditions of the catalytic activity optimum than in an aqueous solution[89]. This implies that the polarity of the medium in which the active centre of the solubilised enzyme is located is significantly lower than the polarity of the aqueous solution[90].

On the other hand, the appearance of "superactivity" can also be caused by conformational changes in the enzyme molecule when it is incorporated in the inverted micelle. Thus, under the conditions of the catalytic activity optimum, a minimum is observed in the curve representing the dependence of the frequency of rotation ν of the spin label in the α-chymotrypsin active centre on w_0 (Fig.3), i.e. there is a minimum in the conformational mobility of the label. The circular dichroism spectra have led to the conclusion[40] that there is an increase of the rigidity (degree of helical configuration) of the α-chymotrypsin molecule solubilised by inverted AOT micelles in iso-octane (the region where $w_0 \cong 10$). The increased conformational rigidity of the enzyme molecule for $w_0 \cong 10$ can apparently be explained by the fact that under these conditions the diameter of the inner cavity of an empty inverted AOT micelle[21] is close to the dimensions of the α-chymotrypsin molecule (40 × 40 × 50 Å).[91]

Another example is provided by horse radish peroxidase solubilised by inverted AOT micelles in octane. Fig.4 shows that the optimum value of k_{cat} greatly exceeds the activity manifested by the enzyme in aqueous solution (dashed line). Furthermore, Fig.4 shows that the optimum value of k_{cat} increases with decrease of the surfactant concentration (with decrease of the area of the interface) and in the limit reaches values hundreds of times greater than the catalytic activity of the peroxidase in aqueous solution[59].

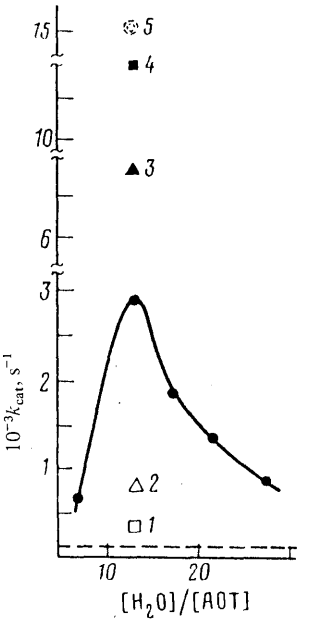


Figure 4. Dependence of the first-order rate constant k_{cat} for the peroxidase-catalysed oxidation of pyrogallol by hydrogen peroxide on the degree of hydration of the surfactant in the AOT (0.1 M)–octane–water (0.025 M phosphate buffer, pH 7.0) system at 26 °C.[59] The rate constants k_{cat} were measured for a fixed degree of hydration $[H_2O]/[AOT] = 13$ at different surfactant concentrations: *1*) 0.5 M AOT; *2*) 0.3 M AOT; *3*) 0.03 M AOT; *4*) 0.03 M AOT + 0.1 M imidazole; *5*) k_{cat} found by extrapolation to zero surfactant concentration. Dashed line—the value of k_{cat} in aqueous solution.

The "superactivity" of the enzyme solubilised by inverted micelles is so far a fairly rare phenomenon. In most cases the catalytic activity of enzymes under normal conditions is close to that observed in aqueous solution (for example in the

case of horse liver alcohol dehydrogenase[39,53], trypsin[45], and pyrophosphatase[57,87]). This fact is consistent with the results of spectroscopic studies[37,39,44–46,54–56,88], according to which the conformation of the protein molecules solubilised by inverted micelles is usually in the main identical with that observed in aqueous solution.

However, it must be emphasised that the relation between the conformational (according to spectroscopic data) and catalytic characteristics of enzymes is not always unambiguous. For example, the catalytic activity of lysozyme solubilised by inverted AOT micelles in iso-octane approaches under optimum conditions that observed in aqueous solution, although the conformation of this enzyme undergoes significant changes after its incorporation into the inverted micelle according to circular dichroism data[41]. On the other hand, spectroscopic characteristics of another enzyme, horse radish peroxidase, hardly change on solubilisation by inverted AOT micelles[46,59], while the optimum catalytic activity of the solubilised peroxidase greatly exceeds that manifested by the same enzyme in aqueous solution (Fig.4). The interpretation of spectroscopic data for solubilised enzymes must therefore be treated with caution.

The Influence of the pH

The rates of enzymic reactions and the kinetic parameters describing them in most cases depend on the pH (see, for example, Berezin and Martinek[1]). When an enzymic reaction was transferred from an aqueous solution to a system of inverted surfactant micelles, significant shifts of the pH profiles were observed[37,40,41,45,52,54,87]. This phenomenon is due to different causes. Firstly, the use of ionogenic surfactants, forming a charged layer (electrical double layer) around the enzyme molecule, can lead to a local shift of the pH (as a function of the sign of the charge of the ionic groups and the degree of hydration of the surfactant molecule). The apparent shift of the pH (and correspondingly of the effective pK) is in this case usually 1–2 units (see the section above dealing with the micromedium in the inner cavities of inverted micelles). Secondly, the acid–base properties of the ionogenic groups of the enzymes solubilised in the inverted micelles can vary with their microenvironment (for example, on partial dehydration). It is well known that the dehydration of ionic groups, which occurs when an aqueous solution is replaced by an aqueous organic solution or a purely organic solution, leads to changes in the pK of the ionic compounds by an amount up to several units[92]. Finally, it is necessary to take into account the possibility of a conformational change in the enzyme on solubilisation, which can also alter the observed pK of its ionogenic groups, including the functional groups involved in the enzymic reaction.

VI. SUBSTRATE SPECIFICITY OF SOLUBILISED ENZYMES

The change in the specificity of the enzyme as a result of its solubilisation can be both true, i.e. associated with a change in the catalytic properties of the enzyme itself, and apparent, i.e. caused by a change in the observed Michaelis constant, which depends, as can be seen from Eqn.(13), on the distribution of the substrate in the inverted micelle system (i.e. on the local concentration of the substrate around the solubilised enzyme molecule.

A change in the true substrate specificity has been established for pancreatic lipase, which catalyses the hydrolysis of the glycerol esters of aliphatic acids[61]. Namely, whereas in aqueous solution k_{cat} for the hydrolysis of tributyrin is greater by a factor of ~2 than for triolein[93], in the AOT inverted micelle system in octane k_{cat} for triolein actually exceeds k_{cat} for tributyrin by a factor greater than 15.[61] This means that the transition from an aqueous solution to the inverted micelle system is accompanied by a significant shift of the true substrate specificity of the lipase in favour of high-molecular-weight substrates.

A striking example of a change in the substrate specificity of an enzyme due to the substrate distribution effects is provided by the oxidation of aliphatic alcohols catalysed by horse liver alcohol dehydrogenase in the AOT inverted micelle system in octane[53]. Fig.5 shows that the transition from an aqueous solution to the inverted micelle system is accompanied by a shift of the maximum on the curve describing the dependence of the second-order rate constant for this reaction $k_{cat}/K_{M,app}$ on the length of the hydrocarbon chain in the molecule of the alcohol substrate n; it is seen that octanol ($n = 8$) is the optimum substrate in water, while butanol ($n = 4$) is the optimum substrate in a colloidal solution of water in octane. In other words, the substrate specificity of alcohol dehydrogenase, whose measure is in fact the quantity $k_{cat}/K_{M,app}$,[94] changes sharply on passing from an aqueous to a micellar solution.

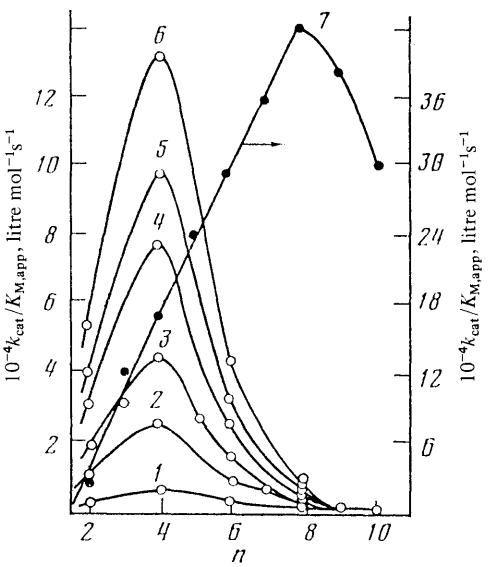


Figure 5. Dependence of the second-order rate constant $k_{cat}/K_{M,app}$ for the oxidation of aliphatic alcohols, catalysed by horse liver alcohol dehydrogenase, on the length of the hydrocarbon chain n in the alcohol substrate molecule[53]. *1*)–*6*) AOT (0.1 M)–octane–water (0.02 M phosphate buffer, pH 8.8) inverted micelle system; $[H_2O]/[AOT]$: *1*) 12.2; *2*) 23.0; *3*) 29.0; *4*) 37.7; *5*) 42.3; *6*) 48.9; aqueous solution (0.02 M phosphate buffer, pH 8.8); temperature 25 °C.

On the other hand, the conformation of the active centre of alcohol dehydrogenase hardly changes in such a transition, which is indicated by spectroscopic data[39] and the fact that the character of the dependence of k_{cat} on n is the same in aqueous solution and in the inverted micelle system[53]. The observed change in substrate specificity is caused[53] by the change in the character of the dependence of $K_{M,app}$ on n

associated with the effects due to the distribution of the alcohol substrate between the micellar and organic phases.

VII. REGULATION OF THE CHEMICAL EQUILIBRIUM IN INVERTED MICELLE SYSTEMS

The system of hydrated inverted surfactant micelles in an organic solvent in the presence of a not unduly high water content constitutes in essence a two-phase water–organic solvent phase, in which, however, the aqueous phase is "uniformly" distributed (by virtue of the presence of the surfactant) in the bulk of the organic solvent. The characteristics of the shifts in the equilibria of the chemical reactions (including enzymic reactions) in two-phase water–organic solvent systems in the absence of surfactants (i.e. in systems where there is a macroscopic interface between the phases) have been investigated in fair detail[95–102]. The approach[95–100] taking into account the distribution of the reactants between the organic and aqueous phases proved fruitful in the analysis of such systems. In particular, for the simplest reaction A ⇌ B in a two-phase system, the kinetic scheme assumes the following form:

$$\begin{array}{ccc} & \overset{K_W}{} & \\ (A \rightleftharpoons B)_W & & \\ {\scriptstyle P_A}\downarrow\uparrow & & \downarrow\uparrow{\scriptstyle P_B} \\ & \overset{K_{org}}{} & \\ (A \rightleftharpoons B)_{org} & & \end{array} \qquad (15)$$

where K_W and K_{org} are the equilibrium constants of reaction (15) in water and in the organic solvent respectively and $P_A = [A]_{org}/[A]_W$ and $P_B = [B]_{org}/[B]_W$ are the partition coefficients of the reactants between the phases, while the subscripts "w" and "org" refer to the aqueous and organic phases respectively. The expression for the effective equilibrium constant of reaction (15), which is equal to the ratio of the concentrations of the reactants A and B relative to the overall volume of the system, i.e. $K_{eff} = [B]_{tot}/[A]_{tot}$, can be formulated[95–98] as follows:

$$K_{eff} = K_W(1+\alpha P_B)/(1+\alpha P_A) \qquad (16)$$

where $\alpha = V_{org}/V_W$ is the ratio of the volumes of the organic and aqueous phases. In conformity with Eqn.(16), the quantity K_{eff} varies monotonically with increase of α—from $K_{eff} = K_W$ for $\alpha = 0$ to $K_{eff} = K_W P_B/P_A = K_{org}$ for $\alpha \to \infty$ (see, for example, curve *1* in Fig.6).

In the more complex case of a bimolecular reaction A + B ⇌ C + D in a two-phase system, the dependence of K_{eff} on α can have the non-trivial form of a curve with an extremum[96–98]. In other words, in a system of two immiscible solvents the effective equilibrium constant can be higher (or correspondingly lower) than the limiting values characterising the equilibrium in each of the phases.

On passing from a truly two-phase water–organic solvent system to a pseudo-two-phase system of hydrated inverted surfactant micelles in an organic solvent, one may expect, in principle, the appearance of effects associated with the specific influence of the surfactant on the equilibrium position. Effects of this kind have been observed[103] in the oxidation of isobutyl alcohol to isobutyraldehyde catalysed by horse liver alcohol dehydrogenase in a system of inverted AOT micelles in octane:

$$RCH_2OH + NAD^+ \overset{K}{\rightleftharpoons} RCHO + NADH + H^+ . \qquad (17)$$

The pH-dependent equilibrium constant of reaction (17) was investigated:

$$K = \frac{[RCHO]_{eq}\,[NADH]_{eq}}{[RCH_2OH]_{eq}\,[NAD^+]_{eq}} . \qquad (18)$$

The results are presented in Fig.6 in the form of plots of $\lg(K/K_W)$, where $K_W = 2.2 \times 10^{-3}$, against the ratio of the volumes of the organic and aqueous phases V_{org}/V_W.

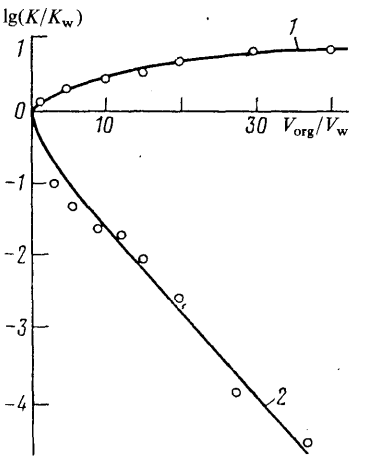


Figure 6. Dependence of the equilibrium constant of reaction (17) on the ratio of the volumes of the organic and aqueous phases[103]; *1*) water (0.02 M phosphate buffer, pH 8.8)–octane two-phase system; *2*) inverted AOT micelle–octane–water (0.02 M phosphate buffer, pH 8.8) system; initial AOT concentration in octane 0.7 M; temperature 20 °C.

In the truly two-phase water–octane system (in the absence of a surfactant), the equilibrium position of reaction (17) can be described by an equation analogous to Eqn.(16), because the coenzymes NAD^+ and NADH are insoluble in octane (their partition coefficients are zero).[96,97] Indeed in this case the dependence of $\lg(K/K_W)$ on the phase volume ratio V_{org}/V_W has the form of a curve with a plateau in conformity with Eqn.(16) (curve *1* in Fig.6). In other words, as the water content in the system diminishes, the equilibrium constant of reaction (17) increases, i.e. the equilibrium shifts to the right (in the direction of the aldehyde). On passing from the two-phase water–octane system to a homogeneous (micellar) solution of water solubilised in octane with the aid of AOT, the character of the dependence of the equilibrium constant on V_{org}/V_W changes sharply (cf. curves *1* and *2* in Fig.6 respectively). Namely an increase of the content of the organic component (octane) in the system leads to a more significant shift of the equilibrium in the presence of the surfactant than in its absence and in addition the shift is in the opposite direction (towards the formation of the alcohol).

The specific influence of AOT on equilibrium (17) is due to the differences between the capacities of the starting materials and reaction products for binding onto the inner surfaces of the inverted micelles formed by the ionic groups of the AOT molecules[103].

It is important to emphasise that the degree of the alcohol–aldehyde conversion in the micellar system can be regulated reversibly by varying the composition of the reaction medium, for example, the water content[103]. Even a slight change in the water content in the system (several tenths vol.%) can then lead to a significant (by an order of magnitude and more) shift of the equilibrium constant (see curve *2* in Fig.6).

VIII. MODELLING OF THE STRUCTURE AND FUNCTION OF BIOLOGICAL MEMBRANES

The idea that inverted micelles constitute an extremely realistic model of biological membrane structures has been frequently stated in the literature[5,104–106]. This hypothesis has been recently confirmed experimentally by Dutch[107–117] and English[118,119] investigators. It was observed that the bilayer membranes frequently contain nonbilayer structures, the so-called lipid particles, which can be clearly distinguished in electron photomicrographs. Investigations showed that these particles consist of associated lipid molecules constructed in the form of inverted micelles and incorporated between the monolayers of the bilayer membrane (Fig.7*a*).

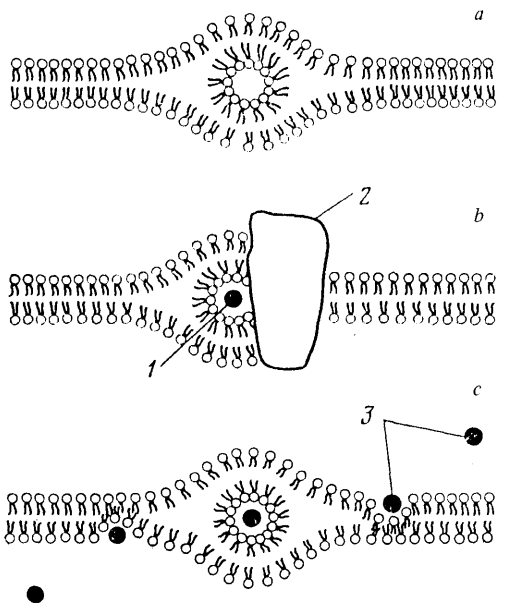


Figure 7. Some of the possible functions of the intramembrane lipid particles (*a*) in a biological membrane[107–122]; *b*) interaction of cytochrome *c* (*1*) with cytochrome oxidase (*2*); *c*) transmembrane transfer of a protein molecule (*3*).

The intramembrane lipid particles together with the intramembrane particles of another kind (for example, protein particles) apparently play an important role in the functioning of biological membranes. This conclusion is based on the fact that membranes characterised by a high metabollic activity (for example, the membranes of mitochrondria and chloroplasts) contain a large number of intramembrane particles, while the relatively inert membranes contain none at all[117]. The most important cell processes such as the coalescence and compartmentalisation of the membranes[110–112, 120,121], exocytosis[111], the transport of lipids through membranes via the "flip–flop" mechanism[113,114], and the transmembrane transport of ions[107,111] proceed via a mechanism similar to that illustrated in Fig.7*c* for protein molecules.

Data[115,116,122] showing that certain proteins, for example, cytochrome *c*, are capable of inducing the formation of inverted micelles in a bilayer membrane, being incorporated at the same time in the inner cavity of such a micelle, are of fundamental importance. It may be that this mechanism plays a significant role in the interaction of cytochrome *c* with the membrane enzyme cytochrome oxidase[116] (Fig.7*b*) and in the transmembrane transport of proteins[115,116,122] (Fig.7*c*).

The functions of the lipid particles and related structures enumerated above have served as a basis of a recently proposed new metamorphic mosaic model of biological membranes[111].

Studies designed to elucidate the role of the nonbilayer lipid particles in membrane processes have only just begun. Nevertheless their first results already show how fruitful can be the employment of inverted micelles as a model of biological membrane structures. We believe[123] that micellar enzymology is fully capable of reflecting the true picture of the functioning of enzymes *in vivo* (particularly when natural lipids are used for the formation of inverted micelles in an organic solvent).

Thus the enzyme "superactivity" [58,59] in inverted micelles compared with the enzyme activity in aqueous solution (see Figs.3 and 4) shows that the catalytic potential of enzymes cannot always be fully elucidated in classical *in vitro* experiments. The most significant differences between catalytic activities will probably be found for the membrane enzymes.

The results obtained in the study of the substrate specificity of pancreatic lipase and alcohol dehydrogenase in the inverted AOT micelle system in octane (Fig.5) justify the expectation of significant differences between the substrate specificities which the enzyme exhibits in a living cell and in aqueous solution in experiments carried out *in vitro*. Furthermore it is possible that the regulating effects observed in the study of the characteristic features of the equilibrium of an enzymic reaction in a micellar system (Fig.6) occur also in a living cell where the content of metabolites might be regulated (with participation of enzymes) by varying the degree of hydration of biological membranes.

IX. APPLIED ASPECTS OF MICELLAR ENZYMOLOGY

The science of chemical reactions and their catalysis by enzymes in inverted micelles is at present in its initial stage and a wide range of problems in this field still awaits solution. However, the experimental data already accumulated indicate the exceptional fruitfulness of this field, which extends and deepens the fundamental knowledge about enzymes and biological membranes.

Micellar enzymology leads to new prospects for the employment of biocatalysis in chemical practice. Thus micellar systems find extensive applications in **organic synthesis**, in the first place for the enzymic transformation of water-insoluble compounds, such as fats, steroids, petroleum products, etc. The possibility of the enzymic hydrolysis of fats has been demonstrated for the action of pancreatic lipase on triglycerides in the "AOT–water–octane" system[61] and a higher catalytic activity of the solubilised enzyme relative to a long-chain less water-soluble substrate was noted. A striking example of the employment of enzymes in inverted micelles for organic synthesis is provided by the work of Dutch investigators[124], who proposed a relatively simple and effective system for the stereospecific production of steroids. This communication should apparently arouse special interest in chemists specialising in synthesis, because, by virtue of the cofactor regeneration system, ordinary molecular hydrogen was used as the reducing agent.

Studies designed to create an energy conversion system have begun to develop in recent years (Berezin and Martinek[2], Chapter XII). A process for the photochemical

formation of hydrogen with participation of an enzyme (a hydrogenase) solubilised by inverted micelles in an organic solvent has been proposed[125].

Enzymes are already used in **analytical chemistry**[2]. Inverted micelle systems lead to new possibilities for the employment of enzymes in the detection of water-insoluble compounds. This is particularly important for the monitoring of the contamination of the environment, which is frequently due to hydrophobic substances such as pesticides and other chemical poisons, the products of incomplete fuel combustion, the waste from chemical industry, etc. The use of enzymes as analytical reagents can lead to the solution also of a more general problem—the creation of reliable test systems for the biological activities of various compounds both water-soluble and water-insoluble. Examples of such analytical systems for the investigation of water-insoluble derivatives of vitamin B_2 have already been successfully realised on the basis of micellar solutions of D-aminoacid oxidase and lipoxygenase[126].

Inverted surfactant micelle systems in organic solvents supplement and extend the methodology of **protein** (enzyme) **chemistry**. They have been used successfully to determine the molecular weights and effective sizes of protein globules[127,128] and also in the thin-layer chromatography of aminoacids[129]. Inverted micelle systems can serve as a universal medium for reactions involved in the **chemical modification of proteins** (enzymes). An envelope of surfactant molecules protects the protein from uncoiling (denaturation) and the presence of the aqueous and organic phases makes it possible to introduce into the reaction both water-soluble and water-insoluble reactants.

In order to impart membranoactive properties to water-soluble proteins, it is necessary to introduce one–two hydrophobic (anchor) groups into the molecule: this procedure has been applied successfully in the treatment with the water-insoluble stearoyl chloride of α-chymotrypsin solubilised by inverted AOT micelles in octane[130]. The converse problem can probably be solved analogously—water-insoluble membrane enzymes can be made hydrophilic by chemical modification.

Although we have consistently emphasised the advantages of employing micellar systems for reactions involving water-insoluble reactants, these systems can prove useful also in many cases regardless of the nature (solubility) of the reactants. From the standpoint of **organic synthesis**, the possibility of regulating the equilibrium position in the catalysed reaction, which should make it possible to carry out reactions whose equilibria in aqueous solution are displaced towards the starting materials (see the relevant reviews[2,100–102]), must be regarded as an important property of inverted micelle systems. The concentration effect and the effects involving an increase of the catalytic activity of enzymes in inverted micelles can increase significantly the sensitivity of **analytical systems**. Indeed it has been shown[131] that, on passing from a traditional aqueous solution to the Brij 96–water–octane system, the sensitivity of the bioluminescence analysis of ATP increases by more than an order of magnitude. Furthermore, the stabilisation of the level of the detected signal is observed in the micellar system, which makes it possible to simplify significantly the entire analytical procedure[131].

The present state and prospects for the practical utilisation of biocatalysis are closely related to the development and improvement of methods for the stabilisation and immobilisation of enzymes[2]. "Molecular immobilisation" has been achieved[132] by the polymerisation of a micellar matrix and/or the components of the inner cavity of the inverted micelle made up of reactants containing a double bond. Protein preparations with an envelope having a specified thickness around each protein molecule were obtained as a result.

It is clear from the achievements and prospects in micellar enzymology that this field of science merits new efforts and investigations. There is every reason to believe that in the course of such investigations new possibilities for the application of micellar enzymology in other fields, not considered in this review, will be discovered and developed.

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Faculty of Chemistry,
Lomonosov Moscow State University

Translated from *Uspekhi Khimii*, 53, 566-582 (1984) U.D.C. 547.541

The Reactivity of Addends in the 1,3-Dipolar Cycloaddition Reaction

Ya.D.Samuilov and A.I.Konovalov

The influence of donor-acceptor interactions and localisation energies on the reactivity of addends in the 1,3-dipolar cycloaddition reaction is examined. It is shown that the interactions between the symmetric frontier orbitals and between the antisymmetric frontier orbitals are qualitatively different in $(4\pi + 2\pi)$-cycloaddition reactions. The effects arising as a result of the interaction of the symmetric frontier orbitals lead to an alteration of the position of the transition state on the potential energy surface for the reaction and increase the sensitivity of the 1,3-dipolar cycloaddition reactions to localisation effects.
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I. INTRODUCTION

The 1,3-dipolar cycloaddition reaction has been vigorously investigated in the last few decades. Interest in this field of study can be accounted for primarily by the fact that a wide variety of heterocyclic compounds, many of which have found extensive application, can be synthesised in a single stage under mild conditions with the aid of the 1,3-dipolar cycloaddition reaction. The theoretical ideas developed in the course of the investigation of this reaction not only promote the understanding of its mechanism and a number of fine details of intermolecular interactions but can also be used successfully in the study of other reactions. The enormous amount of experimental data on the 1,3-dipolar cycloaddition reaction, including the results of kinetic and preparative experiments, have now been surveyed in a series of reviews[1-9].

Both single-stage and two-stage mechanisms have been proposed for the 1,3-dipolar cycloaddition reaction. There is controversy in the literature concerning the type of mechanism which actually operates[10-13]. However, characteristic features of the 1,3-dipolar cycloaddition reactions such as the low sensitivity of the reaction rates to a change in the nature of the solvent[14-16], the weak influence of the substituents in the addends on the reactivity[17-20], the high negative activation entropies, low activation enthalpies, and large negative activation volumes[21], the exceptionally rigorous observation of the *cis*-principle,[22] and the kinetic isotope effects[23-25] agree to a large extent with a synchronous mechanism.

Quantum-chemical calculations of the potential energy surfaces for 1,3-dipolar cycloaddition reactions also indicate a synchronous mechanism of this process[26-34].

There have been reports that the reactions of diazomethanes with dipolarophiles having pronounced electron-accepting properties result in the formation of radical-ions[35-38] but so far it is impossible to solve unambiguously the problem of the role of these species in the reaction.

One of the most important tasks in the study of the 1,3-dipolar cycloaddition reaction is the discovery of factors which determine the reactivity of the addends. These data are essential for the prediction of the reactivity of systems, periselectivity, and stereoselectivity.

The present review is devoted to the consideration of the most important factors responsible for the reactivity of various 1,3-dipole–dipolarophile pairs. Analysis of kinetic data leads to the conclusion that a fairly complete description of the reactivities of such systems is possible only when account is taken simultaneously of the donor–acceptor interactions and the localisation effects. The existence of qualitative differences in the character of the interaction of the symmetric and antisymmetric frontier orbitals of the reactants in the 1,3-dipolar cycloaddition reaction has been established.

II. THE INFLUENCE OF DONOR–ACCEPTOR INTERACTIONS ON THE REACTIVITY OF THE ADDENDS IN THE 1,3-DIPOLAR CYCLOADDITION REACTION

It is nowadays believed that the reactivity of the addends in the 1,3-dipolar cycloaddition reaction depends mainly on the character of the intermolecular donor–acceptor interactions. Stabilisation energies are used for the comparative assessment of the donor–acceptor interactions[39-46]. They are calculated by methods of perturbation theory from the following formula:

$$\Delta E = 2\sum_{t}^{\text{occ}}\sum_{l}^{\text{unocc}} \frac{(C_t^{(l)}C_u^{(l)}\gamma_{tu} + C_{t'}^{(l)}C_{u'}^{(l)}\gamma_{t'u'})^2}{\varepsilon_{a_t} - \varepsilon_{b_l}} + 2\sum_{k}^{\text{occ}}\sum_{j}^{\text{unocc}} \frac{(C_t^{(j)}C_u^{(k)}\gamma_{tu} + C_{t'}^{(j)}C_{u'}^{(k)}\gamma_{t'u'})^2}{\varepsilon_{b_k} - \varepsilon_{a_j}}$$

where C_t are the coefficients of the atomic orbitals in the molecular orbital of the 1,3-dipole, C_u are the coefficients of the atomic orbitals in the molecular orbital of the dipolarophile, γ are interaction integrals, and ε are the energies of the molecular orbitals of the non-interacting systems. The summation is carried out over all possible combinations of the orbitals.

However, this formula is rarely used in specific calculations. In the interpretation of the experimental reactivity data in terms of stabilisation energies, it is usually sufficient to restrict the treatment to allowance for the interaction of the frontier orbitals and it is possible to neglect the differences between the coefficients of the atomic orbitals of the reaction centres[44,46,47]. As a result, the following simple expression is obtained for the stabilisation energy:

$$\Delta E = K\left(\frac{1}{\epsilon_{\text{HOO}}^{\text{1,3-dip}} - \epsilon_{\text{LUO}}^{\text{dip}}} + \frac{1}{\epsilon_{\text{HOO}}^{\text{dip}} - \epsilon_{\text{LUO}}^{\text{1,3-dip}}}\right).$$

Further simplifications in this formula may be associated with allowance for the relative disposition of the frontier orbitals of the addends. Sustmann[39] isolated three types of 1,3-dipolar cycloaddition reactions (Fig.1).

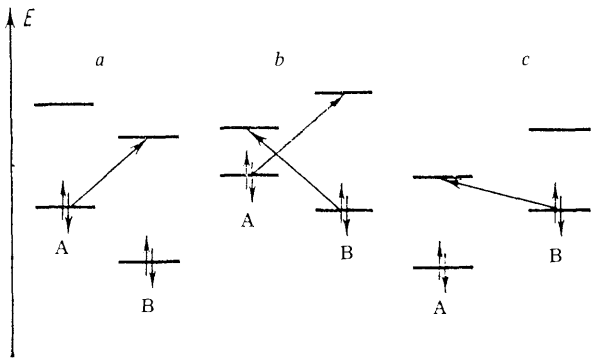


Figure 1. The relative disposition of the energy levels of the frontier orbitals of the addends in the 1,3-dipolar cycloaddition of the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively (*a*), of the "neutral" type (*b*), and of the type where the 1,3-dipole and dipolarophile are the acceptor and donor respectively (*c*); A = 1,3-dipole; B = dipolarophile.

(1) The 1,3-dipole and the dipolarophile are the donor and acceptor respectively. In this case the interaction between the highest occupied orbital (HOO) of the 1,3-dipole and the lowest unoccupied orbital (LUO) of the dipolarophile is dominant.

(2) The "neutral" type. In this case the energy levels of the frontier orbitals of the 1,3-dipole are arranged symmetrically relative to the energy levels of the frontier orbitals of the dipolarophile.

(3) The 1,3-dipole and the dipolarophile are the acceptor and donor respectively. Reactions of this type obtain when the interaction between the lowest unoccupied orbital of the 1,3-dipole and the highest occupied orbital of the dipolarophile is dominant.

The usefulness of the above classification of the 1,3-dipolar cycloaddition reactions has been confirmed by numerous experimental data on the reactivity of the addends in the 1,3-dipolar cycloaddition reactions involving diazomethanes[48–52], nitrile imines[17], nitrile oxides[19,53,54], azides[55,56], etc. Fig.2 presents the dependence of the reactivities of a series of dipolarophiles in the 1,3-dipolar cycloaddition reactions with diazoacetic ester and dimethyl diazomalonate[50] on the ionisation potentials of alkenes. The figure shows that the type of reaction varies with the donor–acceptor characteristics of the dipolarophiles.

However, these and similar correlations may not be associated with a specific relative disposition of the energy levels of the frontier orbitals of the addends in the 1,3-dipolar cycloaddition reaction. Data on the reactivity of *C*-benzoyl-*N*-phenylnitrone in condensations with various dipolarophiles are of interest from this point of view. *C*-Benzoyl-*N*-phenylnitrone is a fairly powerful electron-accepting compound, its electron affinity is 1.0 eV, and its ionisation potential is 10.2 eV.[57] According to theoretical postulates, one might therefore expect that the type of reaction of this nitrone varies readily as the electron-donating character of the dipolarophile is altered.

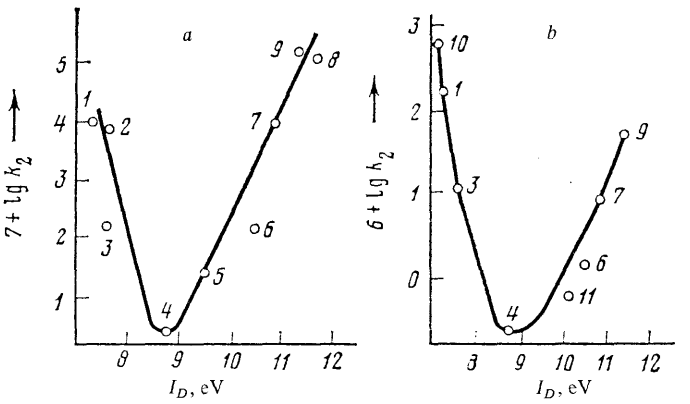


Figure 2. Dependence of the reactivities of diazoacetic ester (*a*) (toluene, 80 °C) and dimethyl diazomalonate (*b*) (mesitylene, 110 °C) in the 1,3-dipolar cycloaddition reaction on the ionisation potentials of the dipolarophiles[50]: *1*) pyrrolidinocyclohexene; *2*) 2-diethylamino-1-methylacetylene; *3*) 1,1-dimethyl-2-pyrrolidinoethylene; *4*) butyl vinyl ether; *5*) dec-1-ene; *6*) styrene; *7*) acrylonitrile; *8*) tetracyanoethylene; *9*) dimethyl acetylenedicarboxylate; *10*) pyrrolidinocyclopentene; *11*) methyl *trans*-crotonate.

In order to test this hypothesis, a kinetic study was made of the reactions of benzoylnitrone with a series of vinyl compounds (Table 1).[57,58] A symmetrical disposition of the energy levels of the frontier orbitals of the addends is attained in the reaction with acrylonitrile (Fig.3). However, the reduced reactivity of dipolarophiles with weaker electron-accepting properties than those of acrylonitrile shows that the entire reaction series belongs to the first type (where the 1,3-dipole and the dipolarophile are the electron donor and acceptor respectively).

Table 1. The reactivities of *C*-benzoyl-*N*-phenylnitrone in the 1,3-dipolar cycloaddition reactions with vinyl compounds (toluene, 20 °C).

Dipolarophile	$10^4 k_2$, litre mol^{-1} s^{-1}	lg *A*	E_A, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
Acroleine	107.3	2.3	23	210
Acrylic acid	90.0	4.6	38	165
Methyl acrylate	44.6	5.4	44	150
Acrylonitrile	28.2	4.9	42	160
Allyl alcohol	14.9	3.9	39	179
Allyl methyl ether	1.4	8.3	69	94

In the reactions of *C*-benzoyl-*N*-phenylnitrone with styrene, the interaction between the lowest unoccupied orbital of the 1,3-dipole and the highest occupied orbital of the dipolarophile is much stronger than the interaction between the other two frontier orbitals (Fig.4). The reactions of styrenes with this nitrone should proceed in accordance with the third type (where the 1,3-dipole and the dipolarophile are the electron acceptor and donor respectively), but kinetic data have shown that the reactivity of arylethylenes determines the interaction between the highest occupied orbital of the nitrone and the lowest unoccupied orbital of the dipolarophile and the reactions proceed in accordance with the first type (with the 1,3-dipole and

dipolarophile as the electron donor and acceptor respectively),[58] this being confirmed by the correlation between the reactivities and the reciprocals of the differences between the ionisation potential of the nitrone and the electron affinities of the styrenes (Fig.5). Changes in the type of reaction are also not observed in the reactions of *C*-benzoyl-*N*-phenylnitrone with dipolarophiles having stronger electron-donating properties than styrenes, namely dipolarophiles such as aryl vinyl ethers[63] and aryl vinyl selenides[58]. Only in reactions with electron-donating dipolarophiles such as α-piperidinylstyrenes was it possible to observe a change in the type of reaction[63]. In this case a correlation is observed between the reactivities and the reciprocals of the differences between the ionisation potentials of the enamines and the electron affinity of *C*-benzoyl-*N*-phenylnitrone (Fig.6), which is evidence that the reaction proceeds in accordance with the third type (where the 1,3-dipole and the dipolarophile function as the electron acceptor and donor respectively).

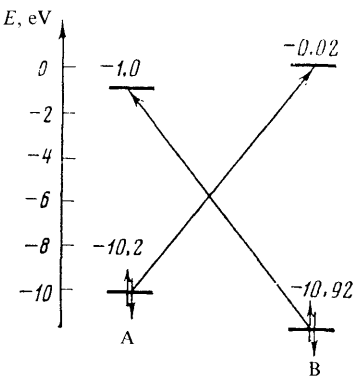


Figure 3. The relative disposition of the energy levels of the frontier orbitals of *C*-benzoyl-*N*-phenylnitrone (A) and acrylonitrile (B). The electron affinity and ionisation potential of acrylonitrile are based on the data of Houk and Munchausen[59].

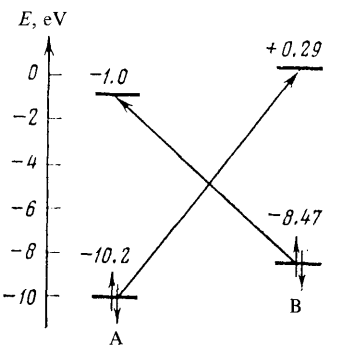


Figure 4. The relative disposition of the energy levels of the frontier orbitals of *C*-benzoyl-*N*-phenylnitrone (A) and styrene (B). The electron affinity and the ionisation potentials are based on the data of Hush and Pople[60] and Gurvich et al.[61] respectively.

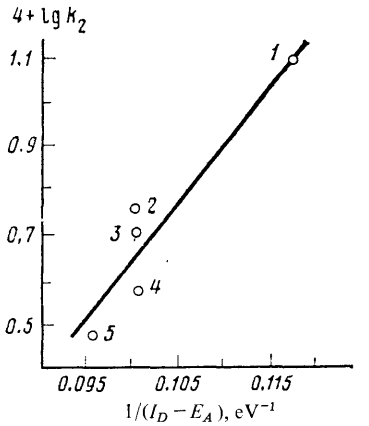


Figure 5. Dependence of the reactivity of *C*-benzoyl-*N*-phenylnitrone in the 1,3-dipolar cycloaddition reaction with styrenes of the type $R-C_6H_4-CH = CH_2$ [58] on the reciprocal of the difference between the ionisation potential of the 1,3-dipole and the electron affinity of the dipolarophile (toluene, 20 °C). The electron affinities of the styrenes were taken from Samuilov et al.[63]; R: *1*) *p*-NO_2; *2*) *p*-Br; *3*) *p*-Cl; *4*) H; *5*) *p*-CH_3O (r = 0.920).

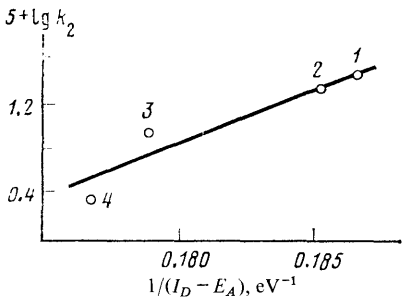


Figure 6. Dependence of the reactivity of *C*-benzoyl-*N*-phenylnitrone in the reaction with α-piperidinylstyrenes $RC_6H_4-CN(CH_2)_5 = CH_2$ on the reciprocal of the difference between the ionisation potential of the enamine and the electron affinity of the nitrone (toluene, 25 °C);[63] R: *1*) *p*-CH_3O; *2*) *p*-CH_3; *3*) H; *4*) *p*-Br.

The data presented indicate a clear preference for the interaction between the highest occupied orbital of the 1,3-dipole and the lowest unoccupied orbital of the dipolarophile compared with the interaction between the lowest unoccupied orbital of the 1,3-dipole and the highest occupied orbital of the dipolarophile. The above phenomenon is characteristic also of the Diels–Alder reaction[64–66]. It is of interest to note that even reactions of electron-accepting dienes such as tetrahalogeno-*o*-benzoquinones with styrenes proceed in accordance with the "neutral" diene synthesis[67], although there is no doubt that in such systems the interactions between the highest occupied orbitals of the styrenes and the lowest unoccupied orbitals of the quinones are much more intense than the interaction between the other two frontier orbitals.

It follows from the data presented that the character of the (4π + 2π)-cycloaddition reactions is probably determined by

the interaction between the highest occupied orbital of the four-electron π-system and the lowest unoccupied orbital of the two-electron π-system.

III. QUALITATIVE DIFFERENCES BETWEEN THE EFFECTS ARISING AS A RESULT OF THE INTERACTION OF ANTISYMMETRIC AND SYMMETRIC FRONTIER ORBITALS IN 1,3-DIPOLAR CYCLOADDITION REACTIONS

The above feature of the interaction of the frontier orbitals of the addends in the 1,3-dipolar cycloaddition reaction becomes understandable after more detailed analysis of the structure of the highest occupied orbital of the 1,3-dipole and the lowest unoccupied orbital of the dipolarophile (each of these orbitals is antisymmetric relative to the plane dividing the system in half) compared with the lowest unoccupied orbital of the 1,3-dipole or the highest occupied orbital of the dipolarophile (symmetric orbitals). The interactions of the frontier orbitals of these pairs lead to qualitatively different effects[68,69].

The formation of a chemical bond requires that the electron density be concentrated during the reaction in the space between the reaction centres. In the case of the synchronous mechanism, this condition is fulfilled for the antisymmetric frontier orbitals (Fig.7). The changes in the coordinates of the atomic nuclei of the interacting centres are in this case such that they promote the occurrence of the reaction. When symmetric frontier orbitals interact, a less favourable situation arises. Cross interactions lead to the localisation of the electron density in the inner part of the intermolecular space. Synchronous changes in the atomic coordinates of the reaction centres do not promote the occurrence of the reaction in this instance. Therefore, even in those cases where the energies of the symmetric frontier orbitals of the addends are fairly similar, nevertheless the antisymmetric orbitals are apparently responsible for the occurrence of the 1,3-dipolar cycloaddition reaction. From this standpoint, it becomes clear that the decisive influence, noted above, on the reactivity by the character of the interaction of the antisymmetric frontier orbitals rest on an entirely well-founded theoretical basis.

We may note an important consequence of the qualitative differences in the character of the interaction of the antisymmetric and symmetric frontier orbitals. When the interaction of the lowest unoccupied orbital of the 1,3-dipole and of the highest occupied orbital of the dipolarophile makes a significant contribution to the stabilisation energy, the contribution by the interaction between the other frontier orbitals can depend on the degree of localisation of the electrons in the reaction centres, which can lead to an alteration of the position of the transition state on the potential energy surface for the reaction and to its shift towards the adduct.

An approach to the interpretation of the reactivities of the addends in the 1,3-dipolar cycloaddition reaction in terms of localisation energies has been available[70,71] but has not come to be widely used. We believe that two approaches, based on the concepts of the stabilisation and localisation energies respectively, supplement one another. In estimating the stabilisation energies, no account is taken of the energy expenditure necessary for the localisation of electrons on the reaction centres. The two approaches describe different aspects of the process in which the transition state is established. An exact description of the reactivity in the 1,3-dipolar cycloaddition reaction is therefore possible only when both effects are taken into account.

In typical Diels–Alder reactions of the first type (where the diene and the dienophile are the electron donor and acceptor respectively) the symmetric frontier orbitals interact only slightly. The influence of the electron localisation effects on the reactivity is therefore insignificant in these reactions. The presence of heteroatoms more electronegative than carbon in the 1,3-dipoles leads to an appreciable enhancement of the electron-accepting properties of these systems[72]. An increased sensitivity to localisation effects should therefore be characteristic of the 1,3-dipolar cycloaddition reactions as a whole.

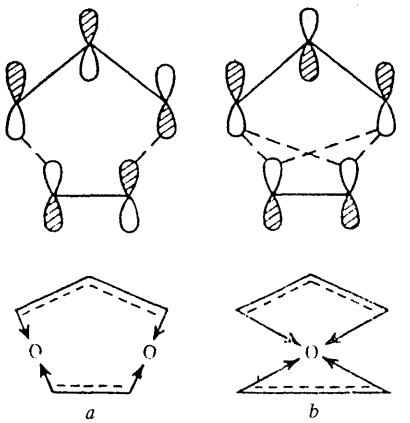


Figure 7. The frontier orbitals in the 1,3-dipolar cycloaddition reaction; *a*) the highest occupied orbital of the 1,3-dipole and the lowest unoccupied orbital of the dipolarophile (antisymmetric orbitals); *b*) the lowest unoccupied orbital of the 1,3-dipole and the highest occupied orbital of the dipolarophile (symmetric orbitals).

Correlations are possible in many instances between the stabilisation and localisation energies[73–75]. However, they are not general. Therefore, in interpreting reactivity, it is necessary to estimate each factor separately.

The localisation energies for the addends can be calculated by quantum-chemical methods. They can be estimated also with the aid of the enthalpies of the corresponding reactions, because the localisation energies and the enthalpies of reaction are linearly related[76].

The dependence of the position of the transition state on the potential energy surface on the character of the donor–acceptor properties of the addends has been discussed[71,77]. On the basis of simple geometrical constructions, the authors of the above studies concluded that an increase of the strength of the intermolecular donor–acceptor interactions leads to a shift of the transition state towards the adduct. We believe that this conclusion is insufficiently well-founded. In the general case donor–acceptor interactions leads to effects stabilising the transition state, which implies that the transition state can be established with a lower degree of formation of new bonds, which corresponds to a shift of the position of the transition state towards the addends.

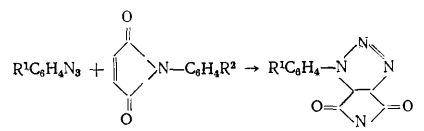
We may note in conclusion that the shift of the position of the transition state on the potential energy surface of the reaction towards the adduct is of the kind indicated in the above studies[71,77] and is associated with the characteristics of the symmetric frontier orbitals of the addends, which do not favour the reaction.

IV. THE INFLUENCE OF LOCALISATION EFFECTS ON THE REACTIVITY OF THE ADDENDS IN 1,3-DIPOLAR CYCLOADDITION

It is clear from the above analysis that the 1,3-dipolar cycloaddition reaction should be characterised by an increased sensitivity to changes in the localisation energies of the addends. When this factor is taken into account, certain anomalies observed for this reaction become understandable. Thus, it is known that 2,4,6-trimethylbenzonitrile oxide gives the "neutral" 1,3-dipolar cycloaddition reaction with styrenes[78]. The enhancement of the electron-accepting character of the dipolarophile should intensify the interaction between the antisymmetric frontier orbitals of the reactants and these reactions should proceed in accordance with the type where the 1,3-dipole and dipolarophile are the donor and acceptor respectively. However, kinetic study of the reactivity of *N*-arylmaleimides (dipolarophiles containing two carbonyl groups at the reaction centres, which ensures pronounced electron-accepting properties of these compounds) in the reaction with 2,4,6-trimethylbenzonitrile oxide[79] has shown that the influence of the substituents is manifested only slightly and the course of the reaction is inconsistent with the expected pattern. This result is not associated with the characteristic features of the transfer of electronic effects in the imides to the reaction centre via the bridging nitrogen atom; this has been confirmed in Diels–Alder reactions with imides, which proceed in accordance with the type where the diene and dienophile function as the donor and acceptor respectively[80,81], in which the accelerating influence of the electron-accepting substituents in the imides and the inhibiting effect of the electron-donating substituents is clearly manifested. Furthermore, the study of the polarographic reduction of *N*-arylmaleimides [82,83] also failed to reveal any characteristic features in the transfer of electronic effects to the multiple bond.

The unusual behaviour of *N*-arylmaleimides in the reaction with 2,4,6-trimethylbenzonitrile oxide is in all probability associated with the fact that the localisation energy increases with enhancement of the electron-accepting character of the substituents in these dipolarophiles[76]. In the reactions with imides, which proceed, according to the classification based on allowance for the donor–acceptor properties alone, in accordance with the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively, there is therefore a possibility of cases where the substituents do not exert an appreciable influence on the reactivity or this influence diminishes with enhancement of the electron-accepting character of the dipolarophiles.

Kinetic data for the reactivity of aryl azides in the 1,3-dipolar cycloaddition reaction with *N*-arylmaleimides are of interest in this connection[84]:



(I)–(III) (IV)–(IX)

R^1=*p*-CH_3O (I), H (II), *p*-NO_2 (III), R^2=*p*-$(CH_3)_2N$ (IV), *p*-CH_3O (V), *p*-CH_3 (VI), H (VII), *p*-Br (VIII), *p*-NO_2 (IX)

Fig. 8 illustrates the correlation between the reactivity of aryl azides in the reaction with arylmaleimides and the Hammett σ constants. It is seen that in the reactions of the azide (I) with the imides (IV)–(IX) there is a tendency towards an increase of the rate of reaction with enhancement of the electron-accepting character of the imides. In the reactions of the azide (II) with the imide (IV)–(IX), both electron-donating and electron-accepting substituents in the dipolarophile favour the reaction. In the case of the azide (III) the electron-donating substituents in the imides increase the rate of reaction, while the electron-accepting substituents reduce it.

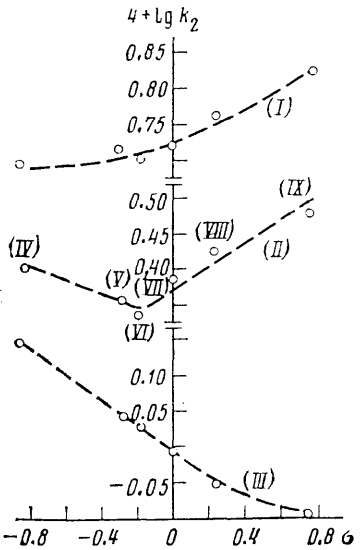


Figure 8. Dependence of the reactivities (lg *k*) of the aryl azides (I)–(III) in the reactions with the *N*-arylmaleimides (IV)–(IX) on the Hammett σ constants (chlorobenzene, 80 °C).[84]

The results obtained can be explained from the standpoint of the donor–acceptor properties assuming that an increase of the electron-donating character of the azide entails a change in the type of reaction from that where the 1,3-dipole and the dipolarophile are the acceptor and donor respectively to that where the roles are reversed. This conclusion conflicts with the reactivities of a series of azides in relation to individual imides: all the reactions indicated proceed in accordance with the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively regardless of the electronic character of the substituents in the dipolarophile.

The observed changes in reactivity can be explained by assuming that the reactivity in the systems investigated is determined not only by the donor–acceptor properties but also by the localisation energies. If the role of these factors varies within the limits of one series, the non-linear correlations described above can arise. From this standpoint, the relative reactivity in reactions with the azide (I) (the azide having the most pronounced electron-donating properties among those investigated) is largely determined by the relative disposition of the energies of the frontier orbitals of the addends.

When the above azide is replaced by phenyl azide (II), which is a weaker electron donor, the role of the antisymmetric frontier orbitals diminishes, while that of the symmetric frontier orbitals increases, which leads to a displacement of the position of the transition state on the potential energy surface towards the adduct. The energy expended on the localisation processes increases and the stabilisation energy diminishes, which results in a decrease of the reactivity of the system. In reactions with imides

containing fairly strong electron-accepting groups in the aromatic ring, the reactivity is largely determined by stabilisation energies. If, on the other hand, arylmaleimides have electron-donating substituents, then the relative reactivity is determined by localisation energies. In the 1,3-dipolar cycloaddition reactions of the azide (III) with the imides (IV)–(XI) the interaction of the symmetric frontier orbitals is most intense for the series considered. The relative reactivity is controlled in this case solely by the localisation energies of the dipolarophiles, as shown by the correlation between the reactivities of the arylmaleimides in the reaction with the azide (III) and the enthalpies of the Diels–Alder reactions of compounds (IV)–(XI) with 1,3-diphenylisobenzofuran (Fig.9). The enthalpies of the reactions considered can be used to estimate the localisation energies of the imides. Fig.9 also presents the point corresponding to maleic anhydride, which is least reactive, although, compared with the imide[86], it is a stronger acceptor[85] and hence should have been more reactive.

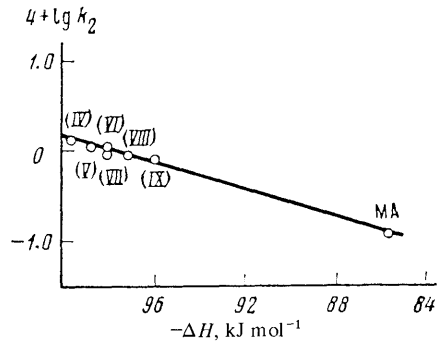


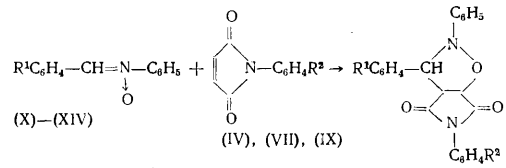
Figure 9. Dependence of the logarithms of the rate constants for the reactions of *p*-nitrophenyl azide (III) with the *N*-arylmaleimides (IV)–(IX) and maleic anhydride on the enthalpies of the reactions of these dipolarophiles with 1,3-diphenylisobenzofuran[84]; MA = maleic anhydride; $r = 0.995$.

The question arises whether the relative changes in reactivity in the above reactions with styrenes are also associated with localisation effects. The change in the electronic character of the substituents in the aromatic ring of styrenes hardly affects the localisation energies of these dipolarophiles, which has been demonstrated by quantum-chemical calculations[87] and has been confirmed by thermochemical experiments[88]. The relative reactivities of styrenes in the 1,3-dipolar cycloaddition reactions are therefore correlated with the stabilisation energies characterising the changes in the donor–acceptor properties.

All these data show that, within the limits of the same series, non-linear correlations can arise. The appearance of these correlations is associated with the change in the relative roles of the donor–acceptor interaction and the localisation effects. The non-linear correlations observed in the study of the 1,3-dipolar cycloaddition reaction have been analysed[89]. The author proposed a new modification of the Hammett equations based on the linearisation of correlations of this type. However, this approach is applicable only in those cases where the reactivity of the addends in several series is determined by at least two factors and the influence of one factor, responsible for the deviation from the Hammett equation, should be the same in all the series, while the influence of the second factor on the reactivity should be correlated with the Hammett σ constants. The applicability of this modification of the Hammett equation is extremely limited. In those cases where the relative roles of the factors determining the reactivity of the addends vary even within the limits of one series, the attempts to linearise the correlations are hardly useful.

The data on the reactivities of nitrones in 1,3-dipolar cycloaddition reactions also cannot be accounted for from the standpoint of the donor–acceptor properties alone. For example, it is known[90] that electron-accepting substituents in dipolarophiles increase their reactivity in reactions with nitrones. It would have been logical to expect that the electron-donating substituents in nitrones also accelerate the reactions. However, kinetic data have shown that both electron-donating and electron-accepting substituents reduce the reactivity in the reactions of *C*-aryl-*N*-phenylnitrones with ethyl crotonate[90]. The existence of such series is altogether incomprehensible from the standpoint of the method of stabilisation energies. In the reactions of *C*-phenyl-*N*-arylnitrones with ethyl crotonate[90], a decrease of the reactivity is observed following the introduction of electron-donating substituents. The hypothesis that these reactions proceed in accordance with the type where the 1,3-dipole and the dipolarophile are the acceptor and donor respectively is unlikely, because even in reactions of an electron-accepting nitrone, such as *C*-benzoyl-*N*-phenylnitrone, with styrenes, which have more pronounced electron-donating properties than ethyl crotonate, an accelerating effect of the electron-accepting substituents in the dipolarophile is observed. The joint kinetic and thermochemical study of the reactions of *C*,*N*-diarylnitrones with *N*-arylmaleimides made it possible to explain the existing phenomena[79,91,92].

Table 2 presents data on the reactivities of *C*-aryl-*N*-phenylnitrones in the 1,3-dipolar cycloaddition reaction with *N*-arylmaleimides and the enthalpies of reaction of these nitrones with *N*-phenylmaleimide:



R¹ = *p*-NO_2 (X), *p*-Br (XI), H (XII), *p*-CH_3O (XIII), *p*-$(CH_3)_2N$ (XIV)

Table 2. The reactivities of *C*-aryl-*N*-phenylnitrones in the 1,3-dipolar cycloaddition reactions with *N*-arylmaleimides and the enthalpies of the reactions of the nitrones with *N*-phenylmaleimide (toluene).[79,92]

Nitrone	*N*-(*p*-dimethylaminophenyl)-maleimide (IV)				$10^3 k_2$ for *N*-phenylmaleimide (VII), litre mol^{-1} s^{-1}	$10^{3*} k_2$ for *N*-(*p*-nitrophenyl)-maleimide (IX) litre mol^{-1} s^{-1}	$-\Delta H^{**}$, kJ mol^{-1}
	$10^{3*} k_2$, litre mol^{-1} s^{-1}	E_A, kJ mol^{-1}	lg *A*	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}			
(X)	1.05	60	7.8	92	1.38	0.92	69.5
(XI)	1.68	54	6.8	109	2.15	1.70	74.9
(XII)	2.54	52	6.6	113	3.20	3.18	82.0
(XIII)	1.66	53	6.6	113	2.01	7.36	72.0
(XIV)	1.12	61	8.0	88	2.15	12.82	63.2

*At 20 °C.
**At 50 °C.

The accelerating effect of the electron-donating substituents in the 1,3-dipole and the inhibiting effect of the electron-accepting substituents, which is characteristic of reactions proceeding in accordance with the type where the

1,3-dipole and the dipolarophile are the donor and acceptor respectively, is manifested in the reactions of the nitrones (X)–(XIV) with the most electrophilic imide (IX). In this case the reactivity can be described satisfactorily in terms of the donor–acceptor properties of the addends alone, which is indicated by the correlation between the reactivities of the nitrones (X)–(XIV) and the reciprocals of the differences between the ionisation potentials of the 1,3-dipoles (I_D) and the electron affinities of the dipolarophiles (E_A) (the ionisation potentials of the nitrones have been determined by Samuilov et al.[93]):

$$\lg k = 25.05\ (I_D - E_A)^{-1} - 6.25\ (r = 0.960)$$

As the electron-donating character of the imides becomes more pronounced, the reactivity of the nitrones diminishes after the introduction of both electron-donating and electron-accepting substituents into the C-aromatic ring. The enthalpies of reaction vary analogously. The inclusion of the enthalpies of reaction, which are linearly related to the localisation energies of 1,3-dipoles, in the correlation equations together with the parameter describing the donor–acceptor interactions, makes it possible to describe the reactivity correctly in this instance. The correlations are based on the following parameters:

(1) for the imide (VII):

$$\lg k = 6.512\ (I_D - E_A)^{-1} - 0.019\ \Delta H - 5.016\ (r = 0.981)$$

(2) for the imide (IV):

$$\lg k = 0.662\ (I_D - E_A)^{-1} - 0.021\ \Delta H - 4.44\ (r = 0.938)$$

In terms of the sign of the coefficient of the reciprocal of the difference between the ionisation potential of the nitrone and the electron affinity of the imide, all the series investigated belong to reactions of the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively. As the electron-donating character of the imide becomes more marked, i.e. as the interactions between the antisymmetric frontier orbitals are weakened and the interactions between the symmetric orbitals are intensified, the role of the localisation effects becomes successively more pronounced. Thus, in the series investigated, consecutive changes in the factors determining the reactivities of the compounds are observed.

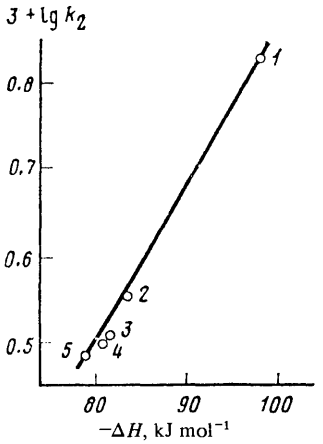


Figure 10. Dependence of the reactivities of *N*-aryl-*C*-phenylnitrones $C_6H_5CH = N(O)-C_6H_4R$ in the reactions with *N*-phenylmaleimide on the enthalpies of reaction (toluene, 20 °C);[92] R: 1) *p*-NO_2; 2) *p*-Cl; 3) H; 4) *p*-CH_3; 5) *p*-CH_3O; $r = 0.990$.

Kinetic and thermochemical study of the reactivities of *C*-phenyl-*N*-arylnitrones with *N*-phenylmaleimide[92] showed (Fig. 10) that the changes in reactivity in this case are parallel to the changes in the enthalpies of reaction, which can be regarded as an indication that the relative reactivities are in this case determined by localisation effects.

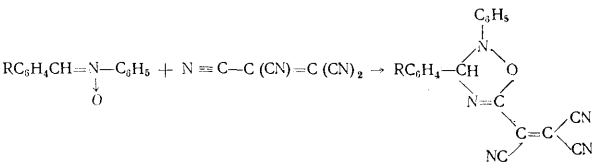
The inconsistency between the electron-donating properties of the nitrones and their reactivities in the 1,3-dipolar cycloaddition reaction with maleic anhydride has been demonstrated[63] (Table 3). In this case the reactivity also varies in parallel with the enthalpies of reaction. This permits the conclusion that in the reactions investigated the localisation effects play an important role, although the reactivity may partly depend also on polar effects[63].

Table 3. The activities of nitrones in the 1,3-dipolar cycloaddition reactions with maleic anhydride, the enthalpies of reaction with toluene, and the ionisation potentials of the nitrones[63].

Nitrone	$10^5 * k_2$, litre mol^{-1} s^{-1}	$-\Delta H_p^{**}$, kJ mol^{-1}	I_D, eV
C-Benzoyl-N-phenylnitrone	3460	84.5	10.2
C,N-Diphenylnitrone	61.1	65.7	7.3
N-Methyl-C-phenylnitrone	8.19	55.6	7.7

*At 20 °C.
**At 50 °C.

In reactions of nitrones with ethyl acrylate[90], *N*-arylmaleimides[79,92,99], and maleic anhydride[63], the influence of the localisation effects on the relative activities is manifested. In conformity with theoretical postulates, it might have been expected that the reactions of nitrones with dipolarophiles more electrophilic than those enumerated above would be controlled solely by the changes in the donor–acceptor properties. One of the most electrophilic dipolarophiles is tetracyanoethylene, whose electron affinity is 2.3 eV.[94] Indeed, the relative reactivities of *C*-aryl-*N*-phenylnitrones in their reactions with tetracyanoethylene are determined by the character of the changes in the electron-donating properties of the 1,3-dipoles (Fig. 11).[93] However, the reactions investigated proceed via the carbon–nitrogen triple bond and not the carbon–carbon double bond[93]:



If these reactions were controlled solely by stabilisation energies, one would expect them to proceed via the carbon–carbon double bond, because the absolute coefficients of the atomic orbitals for the lowest unoccupied molecular orbitals of cyanoethylenes are highest for this bond[59] and in a typical Diels–Alder reaction of the type where the diene and the dienophile are the donor and acceptor respectively the reaction proceeds precisely via this bond[95,96]. A possible cause of the anomalous behaviour of nitrones is the greater strength of the $C_{sp^2}-C_{sp^2}$ π-bond compared with the $C_{sp}-N_{sp}$ π-bond. Thus the strength of the π-bond in ethylene estimated from the difference between the dissociation energies of ethylene and ethane is 314 kJ mol^{-1}, while the similar estimate of the bond strength in hydrocyanic acid is 293 kJ mol^{-1}.[97] The replacement of the hydrogen atoms

in ethylene by cyano-groups results in an additional increase of the strength of the carbon–carbon double bond[76]. The periselectivity of these reactions is apparently determined by the localisation energies.

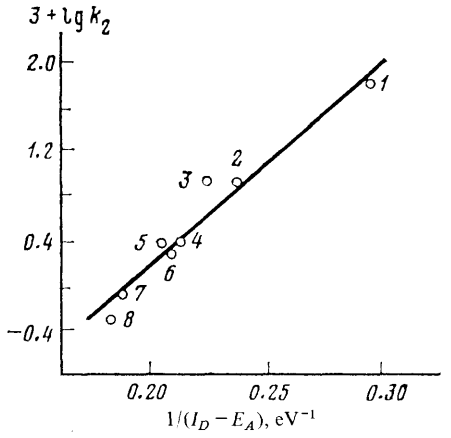


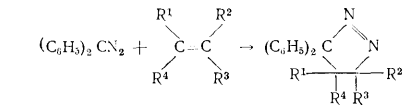
Figure 11. Dependence of the reactivities of *C*-aryl-*N*-phenylnitrones $RC_6H_4CH = N(O)-C_6H_5$ in their reactions with tetracyanoethylene on the reciprocal of the difference between the ionisation potential of the nitrone and the electron affinity of tetracyanoethylene (methylene chloride, 20 °C);[93] R: *1*) *p*-$(CH_3)_2N$; *2*) *p*-CH_3; *3*) H; *4*) *p*-Cl; *5*) *m*-Cl; *6*) *p*-Br; *7*) *m*-NO_2; *8*) *p*-NO_2; $r = 0.951$.

It is of interest to note that, whereas in the reactions of diazomethane[98] and diphenyldiazomethane[99] with tetracyanoethylene products resulting from addition to the carbon–carbon double bond are formed, diazoacetic ester[100] reacts with this dipolarophile via the carbon–nitrogen bond. In the first two instances, the attack is on the site corresponding to the most favourable interaction of the antisymmetric frontier orbitals of the addends, while in the third it is on the centres having the lowest localisation energies. It is remarkable that periselectivity changes in parallel with enhancement of the electron-accepting character of the 1,3-dipole, i.e. with increase of the contribution of the interaction of the symmetric orbitals to the stabilisation energy. The interaction via the carbon–nitrogen triple bond of tetracyanoethylene also takes place in reactions with nitrile sulphides, nitrile oxides[99], and certain other 1,3-dipoles.[101,102]

It was noted above that in a number of instances the stabilisation energy method has been used successfully to interpret the reactivities of dipolarophiles in reactions involving diazomethanes. However, the reactivity of diazo-compounds cannot always be described by taking into account only their donor–acceptor properties. For example, diazomethane is much more reactive in relation to 1,3-dipolar cycloaddition than diphenyldiazomethane[52]. Owing to the increase of the conjugation chain length on passing from diazomethane to diphenyldiazomethane, the energy levels of the frontier orbitals of the 1,3-dipoles approach one another, which can be seen from a comparison of the ultraviolet spectra ($\lambda_{max} = 395$ nm for diazomethane[103] and $\lambda_{max} = 527$ nm for diphenyldiazomethane[37]).

Polarographic data for the anodic oxidation of diazomethane and diphenyldiazomethane indicate an enhancement of the electron-donating character of the compound with increase of the conjugation chain length. Whereas the potential of the first reversible one-electron oxidation half-wave of diphenyldiazomethane at a rotating platinum disc electrode is 0.95 V relative to the saturated calomel electrode[104], for diazomethane the corresponding value is 1.7 V.[105] In view of these data, a higher reactivity of diphenyldiazomethane compared with diazomethane was to be expected. Apparently, the phenylation of diazomethane not only changes the donor–acceptor properties of the 1,3-dipoles but also increases the localisation energies. We may note that an increase of the localisation energies of dienes with increase of the degree of their phenylation had been convincingly demonstrated in earlier studies in relation to the diene synthesis reaction as a result of thermochemical studies of the reactions of butadiene and its phenylated derivative with tetracyanoethylene[106] and 4-phenyl-1,2,4-triazoline-3,5-dione[88]. Presumably a similar phenomenon obtains also in the case of diazomethane.

From the standpoint of the manifestation of qualitative differences between the effects of the interaction of the symmetric and antisymmetric frontier orbitals in 1,3-dipolar cycloaddition reactions, data on the reactivity of diphenyldiazomethane in relation to cyanoethylenes are of interest[107]:



(XV) (XVI)–(XX)

$R^1=R^2=R^3=H$, $R^4=CN$ (XVI); $R^1=R^3=H$, $R^2=R^4=CN$ (XVII); $R^1=R^4=H$, $R^2=R^3=CN$ (XVIII); $R^1=H$, $R^2=R^3=R^4=CN$ (XIX); $R^1=R^2=R^3=R^4=CN$ (XX)

The kinetic parameters of these reactions are presented in Table 4, which also includes the energies of the lowest unoccupied orbitals of the cyanoethylenes (XVI)–(XX) and the localisation energies calculated by the Hückel MO method[108]. It is seen from the data presented that the rate constants and activation energies for the reactions of compounds (XVI) to (XX) are inconsistent with their electron-accepting properties. The cyanoethylene (XVIII) shows the highest reactivity in the reaction with compound (XV), while the dipolarophile (XX), which is a much more powerful electron acceptor than compound (XVIII), reacts more slowly almost by a factor of 100. The variation in the reactivities of cyanoethylenes is also inconsistent with the localisation energy series.

Table 4. Kinetic parameters of the 1,3-dipolar cycloaddition reactions of the cyanoethylenes (XVI)–(XX) with diphenyldiazomethane in chlorobenzene[107] and the energies of the lowest unoccupied orbital (ε_{LUO}) and the localisation energies ($L_{1,2}$) of the dipolarophiles[108].

Cyanoethylene	k_2 litre mol^{-2} s^{-1}, 50 °C	lg *A*	E_A, kJ mol^{-1}	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}	$-\varepsilon_{LUO}$, β	$L_{1,2}$, β
(XVI)	$4.5\cdot10^{-4}$	6.6	47	146	0.6891	2.462
(XVII)	$7.1\cdot10^{-4}$	6.1	51	130	0.6153	2.924
(XVIII)	10^{-2}	—	—	—	0.4826	2.888
(XIX)	13.8	5.2	21	155	0.4008	3.350
(XX)	0.38	4.8	28	159	0.2886	3.776

*At 5 °C.

Thus in the series investigated, the reactivity of the addends is not determined by the preferential influence of a particular factor and is in all probability determined by both factors. This is confirmed by the relation between the activation energies for the reactions of the cyanoethylenes (XVI)–(XX) with diphenyldiazomethane (XV) and the parameters (E_{LUO}, $L_{1,2}$) characterising the electron-accepting and

localisation properties of the dipolarophiles[107]:

$$E_A = -231.8\ (\varepsilon_{LUO} - 0.236\ L_{1,2}) - 250.2\ (r = 0.955).$$

(For a narrow range of compounds, in particular for cyanoethylenes, a linear correlation has been observed between the reciprocals of the differences between the ionisation potentials and the electron affinities and the ionisation potentials or electron affinities[59]. Direct correlations with I_D and E_A have therefore found extensive applications for the description of the reactivities in the series when allowance for the other reactant is unimportant[45].)

In terms of the sign of the constant preceding ε_{LUO}, the series investigated belongs to reactions of the type where the 1,3-dipole and the dipolarophile are the donor and acceptor respectively. The activation energy for the reaction of the cyanoethylene (XVIII) with diphenyldiazomethane calculated from the parameters of the equation is 20 kJ mol^{-1}. In the Diels–Alder reactions of cyanoethylenes with cyclopentadiene and 9,10-dimethylanthracene, which are typical electron-donating dienes, the reactivity of the dienophiles is consistent with their electron-accepting properties[109], while in the reactions of the same compounds with electron-accepting dienes such as substituted phenylcyclones[110] and tetracyclones[111] an appreciable influence of the localisation effects on the reactivities is manifested, although from the standpoint of the donor–acceptor properties these reactions are also of the type where the diene and the dienophile are the donor and acceptor respectively.

Table 5. The enthalpies of activation for the reactions ($\Delta H^{\neq}_{soln}$), the enthalpies of solution of tetracyanoethylene (ΔH^{TCE}_{reactn}) and *C,N*-diphenylnitrone (ΔH^{N}_{reactn}), and the enthalpies of transolvation of the reactants (ΔH^{react}_{solv}) and the transition state (ΔH^{ts}_{solv}) relative to chlorobenzene in the 1,3-dipolar cycloaddition reaction of *C,N*-diphenylnitrone with tetracyanoethylene[112].

Solvent	$\Delta H^{\neq}_{soln}$, kJ mol^{-1}	ΔH^{TCE}_{reactn}, kJ mol^{-1}*	ΔH^{N}_{reactn}, kJ mol^{-1}	ΔH^{react}_{solv}, kJ mol^{-1}	ΔH^{ts}_{solv}, kJ mol^{-1}
Chlorobenzene	56.9	23.1	22.6	0	0
Benzene	78.6	14.9	23.0	−7.8	13.9
Toluene	84.5	9.7	22.6	−13.4	14.2
o-Xylene	109.2	1.4	24.3	−20.0	32.3

*Konovalov et al.[113]

The usual influence of solvents on the reactivity, which can be explained in terms of the qualitative differences between the effects of the interaction of the symmetric and antisymmetric frontier orbitals of the addends, has been observed in the reaction of *C,N*-diphenylnitrone with tetracyanoethylene[112]. The kinetic and thermochemical data for this reaction are presented in Table 5. Evidently, the differences between the activation barriers in different reactions are not only caused by the differences between the solvation energies of the reactants but also depend significantly on the solvation energy of the transition state, the transolvation energy of the activated complex increasing with enhancement of the electron-donating character of the solvent. The observed trends in the transolvation of the transition state become understandable when account is taken of the possibility of a change in the position of the transition state on the potential energy surface.

Enhancement of the electron-donating properties of the solvent reduces the electron-accepting properties of tetracyanoethylene owing to complex formation processes. This entails a weakening of the interaction between the antisymmetric orbitals of the addends and an increase of the contribution to the stabilisation energy by the interaction of the symmetric orbitals. As a result of this, the transition state becomes more localised, i.e. it shifts along the reaction coordinate in the direction of the products. The energy consumed on the localisation increases the energy of the transition state, which parallels the enhancement of the electron-donating properties of the solvent and the diminution of the electron-accepting character of tetracyanoethylene. It is of interest to note that, in the Diels–Alder reaction of tetracyanoethylene with anthracene, the contribution to the stabilisation energy resulting from the interaction of the symmetric orbitals is low and an appreciable influence of the nature of the solvent on the energy of the transition state is not observed[113], which confirms the above point of view.

There is no doubt that the strong influence of solvents on the character of the reaction is possible only in the presence of specific solvation in the system. In those cases where the interaction of the addends with the solvent is weak the rates of 1,3-dipolar cycloaddition reactions change only slightly when the nature of the solvent is altered[14,90].

* * *

The above discussion shows that, for the interpretation of the reactivities of the addends in 1,3-dipolar cycloaddition reactions, it is necessary to take into account not only the donor–acceptor properties of the 1,3-dipoles and dipolarophiles but also the localisation energies of the corresponding reaction centres. While concentrating attention on these two factors, we naturally do not deny the existence of other electronic and steric effects. However, allowance for these factors alone makes it possible in a number of instances to describe the reactivity satisfactorily.

We believe that the qualitative differences in the character of the interaction of the symmetric and antisymmetric frontier orbitals are important. The understanding of the role of these interactions facilitates the prediction of the reactivities of addends in the $(4\pi + 2\pi)$-cycloaddition reaction and makes it possible to carry out a specific search for systems whose reactivity is determined mainly by a particular effect.

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Ul'yanov-Lenin Kazan State University

Translated from *Uspekhi Khimii*, 53, 583-594 (1984) U.D.C. 547.539.4

Advances in the Synthesis of Aromatic Iodo-compounds

E.V.Merkushev

The review presents a compilation of data on the iodination of aromatic compounds published during the last 10-20 years. The synthetic advantages of various methods of preparation of aromatic iodo-derivatives are examined and data concerning the mechanism of direct iodination are presented.
The bibliography includes 127 references.

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I. INTRODUCTION

The expansion of the range of methods of organic synthesis involves both the discovery of new reactions and reagents and a deepening of our knowledge of the chemical properties of compounds already known. The latter applies fully to the chemistry of aromatic iodo-derivatives. For about 100 years, aryl iodides have been used in various organometallic syntheses, mainly in the Ullmann reaction (for the latest reviews on this reaction, see Fanta[1] and Goshaev et al.[2]). A new branch of this by no means complete field of study involves the condensation of copper acetylides with compounds containing a halogen attached to an unsaturated carbon atom (usually with aryl iodides). Further progress in this field is associated with the application of transition metal complexes, particularly palladium complexes (see the relevant reviews[3-6]). Summarising the reactions of halides in the presence of palladium salts, Heck[7] noted the enhanced and frequently uniquely high reactivity of the iodo-derivatives.

One must note the elegant method of generating aryl radicals in the photolysis of aryl iodides discovered by Kharasch and co-workers[8,9]. It must be emphasised that the reaction between aryl iodides and styrenes leads to stilbenes, which are the starting materials for the synthesis (by photochemical dehydrocyclisation) of a wide variety of compounds containing the phenanthrene fragment[10].

It is to be expected that further studies will expand still more the applications of aromatic iodo-derivatives in organic synthesis. One of the causes which has retarded a more extensive involvement of aryl iodides in practical organic synthesis has been the lack of simple and reliable methods of their preparation; the main method for the synthesis of the majority of aryl iodides up to the 1950s involved a multistage synthesis based on the Sandmeyer reaction. However, the studies in the last 10–20 years have led to the discovery of new simple methods which have made aryl iodides quite easily available.

Whereas the methods of synthesis of aromatic bromo-, chloro-, and fluoro-derivatives have been widely described in monographs and have been published periodically in journal reviews, there are no similar publications devoted to aromatic iodo-derivatives with the exception of a short chapter in a monograph[11]. The main aim of this review is to draw the attention of chemists engaged in synthesis to the advances in the synthesis of aromatic iodo-derivatives.

The known methods of synthesis of aryl iodides can be divided into two large groups: direct iodination based on the direct formation of the carbon–iodine bond on substitution of aromatic compounds and indirect iodination involving the initial substitution of hydrogen in the aromatic substrate by an atom or group with its subsequent replacement by iodine. The entire experimental data are examined henceforth on the basis of this classification.

II. DIRECT IODINATION

The vast majority of aromatic compounds, with the exception of a series of amines and phenols whose reactions are not considered in this review, do not interact with molecular iodine in the absence of oxidants. The set of oxidants used in direct iodination reactions was extremely limited up to the 1950s, but studies in recent years have greatly increased their number, which has led to the development of simple and reliable methods of synthesis of iodo-derivatives of different classes.

1. Iodination by the Tronov–Novikov Method

At the beginning of the 1950s, Tronov and Novikov showed that the iodination reaction can be successfully carried out in acetic acid in the presence of nitric and sulphuric acids as oxidants[12-14]. In the course of numerous experiments, it was established that the best results are obtained when mixtures of nitric ($d = 1.4$) and sulphuric ($d = 1.84$) acids are employed. This method was subsequently extended to a wide range of aromatic substrates[15-18] including benzene and its homologues, polynuclear aromatic compounds, oxygen-containing aromatic compounds (ethers, aldehydes, ketones, and carboxylic acids) and aromatic compounds of other classes.

In iodination by the Tronov–Novikov method, the organic substrate is usually dissolved in glacial acetic acid, finely ground iodine is added, and then a mixture of nitric and sulphuric acid is added dropwise with intense stirring (at temperatures ranging from room temperature to the boiling point of glacial acetic acid). In the iodination of reactive aromatic compounds, the acid mixture is diluted with acetic acid[19]. Sometimes, when the reaction is carried out at an elevated temperature, it is useful to add several millilitres of carbon tetrachloride to the reaction mixture in order to wash off the subliming iodine. The reaction is accompanied by the evolution of nitrogen oxides; it can be followed visually from the disappearance of iodine. In order to isolate the reaction products, the reaction mixture is diluted with water in most cases, and the iodo-derivative formed is filtered off.

Iodobenzene (80%), 2-iodo-*p*-xylene (87%), 2,5-di-iodo-*p*-xylene (85%), iodomesitylene (88%), iododurene (100%), di-iododurene (88%), di-iodomesitylene (80%), tri-iodomesitylene (63%), iodopentamethylbenzene (87%), 4,4′-di-iodobiphenyl (68%), 2,7-di-iodofluorene (50%), 2,7-di-iodofluorenone (75%), 2,7-di-iodophenanthrenequinone (50%), 2-iodofluorenone-5-carboxylic acid (65%), as well as many other aromatic iodo-compounds have been obtained by this method.

Iodonitro-derivatives are formed as side products at elevated temperatures[20], which suggested a "single-stage" reaction for the introduction of iodine and nitro-groups into aromatic compounds[21]; studies of the isomeric composition of the products led to the conclusion that iodination takes place initially and is followed by nitration[22]. 4-Iodonitrobenzene (46%), 2-iodo-5-nitro-*p*-xylene (45%), 4-iodo-4′-nitrobiphenyl (50%), and 2-iodo-7-nitrofluorene (61%) have been synthesised successfully by this method[22-25].

Further studies of the oxidative side processes will probably lead to the development of new useful methods, as can be seen from the synthesis of 4,4′-di-iodobenzophenone in 40% yield on iodination of diphenylmethane[26].

2. Iodination in the Presence of Iodic and Periodic Acids

Although iodination in the presence of iodic acid has been known for more than 100 years (see, for example, Kekulé [27]), the extensive possibilities of this reagent as an oxidant in the iodination of a large number of aromatic substrates were demonstrated only in 1960.[28] Subsequently, this reagent was used in the iodination of *p*-xylene and durene[29]. The method is convenient for the iodination of fluorene whose molecule contains the readily oxidisable methylene group[30]; it proved useful also in the iodination of methylated polyphenylenes[31-33].

Periodic acid dihydrate is used in the iodination of alkylbenzenes[34-36]. In particular, satisfactory results have been obtained in the presence of this oxidant in the monoiodination of mesitylene, durene, pentamethylbenzene, 5-t-butyl-1,3-dimethylbenzene, 4-t-butyl-1,2-dimethylbenzene, and even 5-t-butyl-1,2,3-trimethylbenzene, 1,2,4,5-tetraisopropylbenzene, and *p*-di-t-butylbenzene. A critical examination of the methods of synthesis of iodo-derivatives of alkylbenzene led to the conclusion[37] that the above procedure is the most suitable for the introduction of one and two iodine atoms into the alkylbenzene molecule. The efficiency of periodic acid in the iodination of unsubstituted polyphenylenes[38,39], fluoranthene[40], and acenaphthene[41] has been demonstrated.

3. Iodination in the Presence of Peracetic Acid

It was shown in the middle 1960's [42-46] that peracetic acid is an effective oxidant in direct iodination. The method was extended to a wide range of aromatic substrates; particularly good results were obtained for atomatic compounds containing electron-donating substituents.

The study of the reaction mechanism led to the hypothesis that acetyl hypoiodite and its protonated form are the source of electrophilic iodine[44]. Autocatalysis in the iodination of benzene homologues with electron-donating substituents was noted and the authors explained it by the oxidation of the iodo-derivatives formed initially by the corresponding iodoso-derivatives or their acetates in accordance with the following scheme:

$$ArI + CH_3CO_3H \rightarrow ArIO + CH_3CO_2H ,$$
$$ArIO + 2CH_3CO_2H \rightarrow ArI(OCOCH_3)_2 + H_2O .$$

The polyvalent iodine compounds formed are effective oxidants in the oxidation of iodine to acetyl hypoiodite:

$$ArI(OCOCH_3)_2 + I_2 \rightarrow ArI + 2CH_3COO^{\oplus}I^{\oplus}$$

This hypothesis was confirmed by the successful iodination of *m*-xylene in warm acetic acid in the presence of iodosobenzene or phenyliodoso acetate+.

4. Iodination in the Presence of Variable-Valence Metal Chlorides

In 1970 a method was proposed for the direct iodination of aromatic compounds using bivalent copper chloride and an iodine donor (I_2, AlI_3, or $FeI_2.4H_2O$).[47] It was also found that the copper acetate–iodine system is effective for the iodination of azulene[48].

The effectiveness of antimony pentachloride as the oxidant in the oxidation of aromatic compounds in carbon tetrachloride was demonstrated in 1974.[49] It is of interest to note the very high yields of the *p*-isomers, which are respectively 98, 99, and 100% in the case of fluorobenzene, chlorobenzene, and bromobenzene.

5. Iodination by *N*-iodoamides

N-Iodosuccinimide is used successfully in the iodination of fluorene[50] (for the synthesis of the reagent, see Benson et al.[51]). The effectiveness of acid *N*-iodoamides in arene iodination reactions has been demonstrated[52-55]. These reactions are accelerated on catalysis by acids; particularly good results have been obtained using trifluoroacetic acid[55]. The authors believe that trifluoroacetyl hypoiodite is the source of electrophilic iodine in this process.

Trifluoroacetyl hypoiodite was probably first postulated as a source of electrophilic iodine by Henne and Zimmer[56], who demonstrated the effectiveness of the iodine/silver trifluoroacetate system in the iodination of aromatic compounds; an elegant method of synthesis of iodoveratrol was developed on the basis of this procedure[57]. In this reaction, iodine can be successfully replaced by chlorine iodide[58]. It has been shown that in the series of acetyl hypohalites, trifluoroacetyl hypohalites are the most powerful halogenating agents[59].

6. Iodination in the Presence of Phenyliodoso Trifluoroacetate#

An attempt at the coupled addition of iodine and trifluoroacetoxy-groups to the triple bond of tolane, by analogy with iodoacetoxylation by the iodine/phenyliodoso acetate system was made in 1979.[60] However, instead of the expected addition to the triple bond, tolane was oxidised to an α-diketone (benzil). It was found that the oxidation of diarylacetylenes to α-diketones is a general reaction[61]. Together with benzil, *p*-di-iodobenzene, formed as a result of the iodination of iodobenzene whose source was a molecule of phenyliodoso trifluoroacetate, was isolated from the reaction product[62]. Inorganic derivatives of polyvalent iodine (iodic and periodic acid) are widely used as oxidants in direct iodination reactions but organic derivatives of polyvalent iodine have not

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+Bis(acetato-*O*)phenyliodine (Ed.of Translation).

#Bis(trifluoroacetato-*O*)phenyliodine (Ed.of Translation).

been used until recently in preparative organic chemistry, although the possibility, in principle, of iodinating *m*-xylene in warm acetic acid using iodosobenzene or phenyl iodosoacetate was demonstrated as early as 1963.[44] Phenyliodosoacetate has no special advantages over more readily available oxidants in direct iodination reactions; when azobenzene is iodinated in the presence of phenyl iodosoacetate, 4-iodoazobenzene is formed only in insignificant yield[63].

A detailed study of iodination in the presence of phenyliodoso trifluoroacetate showed that, in contrast to phenyliodoso acetate, this reagent is very effective as an oxidant and makes it possible to introduce from one to three iodine atoms into the aromatic ring at room temperature[64–66]. It was found that the iodine/phenyliodoso trifluoroacetate system is effective in the iodination of not only benzenoid compounds but also certain heterocycles[67]. It was discovered that the bromine/phenyliodoso trifluoroacetate system is effective in the bromination of aromatic compounds[60]. Some data on the iodination of aromatic compounds by the iodine/phenyliodoso trifluoroacetate system at room temperature are presented in Table 1.

Table 1. Iodination in the presence of phenyliodoso trifluoroacetate.[66]

Aromatic substrate	Aryl iodide	Yield, %
Benzene	Iodobenzene	72
o-Xylene	4,5-Di-iodo-*o*-xylene	55
m-Xylene	4,6-Di-iodo-*m*-xylene	77
p-Xylene	2,5-Di-iodo-*p*-xylene	65
Mesitylene	Tri-iodomesitylene	84
Durene	Di-iododurene	52
Diphenylmethane	4,4'-Di-iododiphenylmethane	52
Triphenylmethane	4,4',4''-Tri-iodotriphenylmethane	32
Biphenyl	4,4'-Di-iodobiphenyl	87
p-Terphenyl	4,4''-Di-iodo-*p*-terphenyl	93
Chlorobenzene	1-Chloro-4-iodobenzene	61
Bromobenzene	1-Bromo-4-iodobenzene	63
Iodobenzene	1,4-Di-iodobenzene	73
Diphenyl ether	Di(4-iodophenyl) ether	79
Fluorenone	2,7-Di-iodofluorenone	51
Biphenyl-4-carboxylic acid	4-Iodobiphenyl-4'-carboxylic acid	81
Fluorene-9-carboxylic acid	2,7-Di-iodofluorene-9-carboxylic acid	70
Methyl fluorene-9-carboxylate	Methyl 2,7-di-iodofluorene-9-carboxylate	52
Diphenylene oxide	3,6-Di-iododiphenylene oxide	59

On the basis of the data obtained in a ^{19}F NMR study of the iodination of arenes in carbon tetrachloride at room temperature, trifluoroacetyl hypoiodite has been proposed as the iodinating agent:

$$C_6H_5I(OCOCF_3)_2 + I_2 \rightleftarrows C_6H_5I + 2F_3CCOOI;$$
$$ArH + F_3CCOOI \rightarrow ArI + F_3CCOOH\ .$$

It was established that phenyl iodosotrifluoroacetate, prepared beforehand, must be used in the reaction. It can be generated in the reaction mixture *in situ* from phenyl iodosoacetate and trifluoroacetic acid[66].

The iodination reaction takes place at room temperature with aromatic substrates which are not oxidised under the experimental conditions and are more reactive in electrophilic substitution reactions than iodobenzene. The attempt to iodinate nitrobenzene, benzoic acid, and benzophenone led only to *p*-di-iodobenzene as a consequence of the iodination of the iodobenzene formed from phenyliodoso trifluoroacetate.

7. Iodination of Polymers

Reagents on a polymeric support have been recently introduced into practical organic synthesis. From this standpoint, iodine-containing polymers are of special interest since iodine can be readily substituted by another functional group or a reagent with polyvalent iodine can be formed. Compounds containing the iodosochloride [aryliodine dichloride] group in the benzoic acid residue, joined by an ester linkage to a steroid molecule[69], or an iodosofluoride [aryliodine difluoride] group in a polymeric molecule[70], have been used successfully in the selective halogenation of organic compounds. Polystyrene can be iodinated in the presence of iodic acid[71] or iodine pentoxide[72] as oxidants but iodination in the presence of phenyliodoso trifluoroacetate is a more convenient method[73].

8. Introduction of Polyvalent Iodine into the Aromatic Ring

The introduction of the iodo-group into the aromatic molecule on treatment with iodic and sulphuric acids can be classified as a variety of the direct iodination reaction[74]. Together with benzene, halogenobenzenes, benzoic acid, and nitrobenzene can enter into this reaction. The reduction of iodo-derivatives leads to the corresponding aryl iodides. On treatment with iodine tris(trifluoroacetate), it is possible to introduce the $(CF_3COO)_2I$ group[75]. The reduction of aryliodoso trifluoroacetates leads to aryl iodides. Many problems involving the mode of substitution in the benzene ring can be solved in this field. Whereas iodine is *ortho-para* directing, polyvalent iodine exhibits a powerful *meta*-directing effect.

III. INDIRECT IODINATION

The reaction involving the replacement of the amino-group by iodine via diazonium salts has still not lost its importance especially when the amine is commercially available or it is necessary to synthesise an iodide having a specific structure without admixtures of other isomeric iodo-derivatives. The diazotisation of aniline in the presence of iodine[76], which makes it possible to obtain *p*-di-iodobenzene, probably via an intermediate aniline iodination stage, can be classified as a reaction of this type. In this connection it is necessary to point out a publication[77] whose authors claim that the synthesis of iodo-derivatives with the aid of diazonium salts in the presence of crown-ethers has advantages over the classical version of the Sandmeyer reaction. It is of interest to note the thermal stability of aryl iodides; the thermolysis of aryl bromides in the presence of iodine can serve as a preparative method of synthesis of iodo-derivatives[78].

Since, together with primary aromatic amines, aromatic carboxylic acids are the most readily available functional derivatives, the potential possibility of replacing the carboxy-group by iodine is of undoubted interest. A number of methods for the replacement of the carboxy-group (in the form of various derivatives) by iodine have been developed in recent years and will be considered below. Striking advances in the synthesis of aryl iodides were associated with the application of organometallic compounds, particularly thallium derivatives. In addition, reactions involving the decomposition of organic compounds of polyvalent iodine, leading to aryl iodides, have been examined; a series of effective methods of synthesis of polyvalent iodine compounds, which have led to the use of these previously exotic compounds as intermediates in the preparative synthesis of aromatic iodo-derivatives, have also been developed.

1. The Replacement of the Carboxy-Group by Iodine

The catalytic decarbonylation of aromatic carboxylic acid iodides to the corresponding aryl iodides by tris(triphenylphosphine)rhodium chloride was described in 1968.[79] *o*-Diiodobenzene, *o*-chloroiodobenzene, and *m*-di-iodobenzene, which are difficult to obtain by direct iodination, have been obtained in satisfactory yields by the above method. The reaction proceeds under mild conditions and gives rise to high yields of the iodide. The discovery of a relatively simple method of synthesis of aroyl iodides from the corresponding aroyl chlorides and sodium iodide[80] undoubtedly makes the decarbonylation reaction valuable in practice.

It is known that the thermolysis of aroyl peroxides in the presence of iodine can serve as a preparative method of synthesis of aryl iodides; particularly good results have been obtained using the peroxides of nitrobenzoic acids[81].

The Borodin–Hunsdieker reaction has not found extensive applications in the synthesis of aryl iodides but it should be noted that the photolysis of naphthoic acids in the presence of lead tetra-acetate and iodine has led to the corresponding iodonaphthalenes in high yields[82].

2. The Synthesis of Iodo-derivatives Via Organothallium Compounds

As early as the 1940's, Gilman observed[83] that organothallium compounds can be obtained with the aid of thallium trichloride. However, this reaction did not find applications in organic synthesis, probably as a consequence of the insignificant yield and severe conditions. In the 1950's Glushkova and Kocheshkov discovered the reaction involving the direct introduction of thallium into aromatic compounds by thallium tri-isobutyrate at 95–115 °C with formation of arylthallium di-isobutyrates[84–87]; they also demonstrated the ease of the cleavage of the thallium–carbon bond by molecular iodine with formation of iodo-derivatives. However, this reaction has not found synthetic applications, probably because of the difficulties in the introduction of thallium into deactivated aromatic compounds owing to the low electrophilicity of thallium tri-isobutyrate.

In 1969 McKillop and co-workers[88] showed that thallium tris(trifluoroacetate) is an excellent reagent for the introduction of thallium into organic substrates. It may be noted that the method of synthesis of thallium tris(trifluoroacetate) quoted in the well-known book by Fieser and Fieser[89] cannot be reproduced. Fieser and Fieser apparently based their description on a brief communication[88] where it was not stated that a small amount of water is essential for the preparation of thallium tris(trifluoroacetate) from thallium oxide and difluoroacetic acid; this was noted in a subsequent more detailed publication[91]. It has been established[90,91] that treatment of arylthallium bis(trifluoroacetate) with an aqueous solution of potassium iodide constitutes a very simple method of synthesis of aryl iodides:

$$ArH \xrightarrow{Tl(OCOCF_3)_3} ArTl(OCOCF_3)_2 \xrightarrow{KI} ArI$$

Substitution by thallium is usually carried out in trifluoroacetic acid; in the case of substrates sensitive to the action of acids, it is possible to employ acetonitrile. Aromatic compounds are usually substituted by thallium in the course of several minutes at room temperature but deactivated substrates require heating with thallium tris(trifluoroacetate) in boiling trifluoroacetic acid. Some data on the synthesis of aryl iodides via organothallium compounds are listed in Table 2.

Table 2. Synthesis of aromatic iodo-derivatives via organothallium compounds.

Aromatic Substrate	Aryl iodide	Yield, %	Refs.
Benzene	Iodobenzene	96	[91]
Benzene*	1,4-Di-iodobenzene	89	[92]
Benzene*	1,2,4-Tri-iodobenzene	70	[92]
Benzene*	1,2,4,5 Tetraiodobenzene	41	[92]
t-Butylbenzene	1-t-Butyl-4-iodobenzene	93	[91]
o-Xylene	4-Iodo-1,2-dimethylbenzene	98	[91]
m-Xylene	4-Iodo-1,3-dimethylbenzene	100	[91]
p-Xylene	2-Iodo-1,4-dimethylbenzene	91	[91]
Mesitylene	Iodomesitylene	94	[91]
Mesitylene*	Di-iodomesitylene	92	[92]
Mesitylene*	Tri-iodomesitylene	82	[92]
Biphenyl	4-Iodobiphenyl	70	[91]
Naphthalene	1-Iodonaphthalene	60	[91]
Benzoic acid	2-Iodobenzoic acid	76	[91]
p-Toluic acid	2-Iodo-4-methylbenzoic acid	75	[93]
Anisole	4-Iodoanisole	75	[91]
10,10-Dimethylanthrone	1-Iodo-10,10-dimethylanthrone	29	[94]
Dibenzosuberone	4-Iododibenzosuberone	71	[94]
Trifluoromethylbenzene	3-Iodo-1-trifluoromethylbenzene	54	[91]
2,3,5,6-Tetrafluoroanisole**	2,3,5,6-Tetrafluoro-4-iodoanisole	39	[95]
2,3,5,6-Tetrafluorotoluene**	2,3,5,6-Tetrafluoro-4-iodotoluene	77	[95]
1,3,4,5-Tetrafluorobenzene**	2,4,5,6-Tetrafluoro-1-iodobenzene	77	[95]
Pentafluorobenzene**	Pentafluoroiodobenzene	67	[95]
Azobenzene	2-Iodoazobenzene	55	[96]
Azobenzene	2,2'-Di-iodoazobenzene	36	[96]

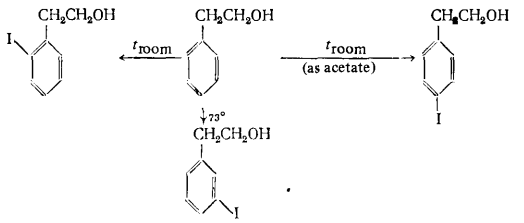
*Iodination in the presence of thallium tris(trifluoroacetate).

**Thallation with thallium tris(trifluoromethanesulphonate).

Glushkova and Kocheshkov[87] noted in an early study the absence of polythallation products when thallium tri-isobutyrate is used. McKillop and co-workers indicated only one instance of polythallation[97]. Studies of substitution by thallium with the aid of thallium tris(trifluoroacetate) showed that, under severe conditions, it is possible to introduce two bis(trifluoroacetoxy)thallium groups into the aromatic ring; after decomposition with potassium iodide, the corresponding di-iodo-derivatives were obtained in an insignificant yield[98]. Deacon and Tunaley[95] showed that thallium tris(trifluoromethanesulphonate) is more electrophilic than thallium tris(trifluoroacetate); with its aid, it is possible to substitute by thallium many deactivated substrates which do not react with thallium tris(trifluoroacetate). Treatment of the thallium compound with an aqueous solution of sodium iodide leads to the corresponding iodides. Substitution by thallium using thallium tris(trifluoroacetate) with subsequent treatment by potassium iodide is used solely for the preparative synthesis of monoiodoarenes. On the other hand, the interaction of aromatic compounds with molecular iodine in the presence of thallium tris(trifluoroacetate) as the oxidant[92] can serve as a method of preparative synthesis of polyiodo-derivatives. Mono-, di-, tri-, and tetra-iodo-derivatives of benzene have been obtained by this method in high yields.

It was found that benzoic acid is substituted by thallium in the *ortho*-position with an unusually high yield (~98%).[88] Further studies[99] established that many oxygen-containing compounds form complexes with the thallium salt in a preliminary step. If intramolecular attack can lead to the formation of a five- or six-membered transition state, then thallium attacks the available *ortho*-position. A similar

discovery was also made for azobenzenes[100]. The arene thallation reaction is reversible[99]; using thermodynamic and kinetic control and also bearing in mind the formation of complexes, it is possible to select conditions under which the required isomer is obtained with the maximum yield[101]:



Subsequently it was shown that diarylthallium trifluoroacetates, readily obtainable from arylthallium bis(trifluoroacetates) on treatment with triethyl phosphite or warm aqueous acetone, react with iodine to form the corresponding aryl iodides in very high yields[102]. This method can be regarded as a procedure for the conversion of aryl bromides or aryl chlorides into the corresponding iodides, since one of the methods of synthesis of diarylthallium compounds consists in the interaction of Grignard reagents with tervalent thallium salts (halides or carboxylates).[103]

3. The Synthesis of Aryl Iodides Via Organomercury Compounds

In 1974 Deacon and Farquharson[104] established that arenes give rise to polymercurated derivatives on fusion with mercury trifluoroacetate. Treatment of these compounds with a solution of bromine and potassium bromide in methanol constitutes an effective method for the synthesis of polybrominated arenes[105]. Polyiodoarenes are formed analogously in high yields on reaction with iodine and potassium iodide in dimethylformamide, while treatment of polymercuriarenes with molecular chlorine gave rise to polychloroarenes[106]. It has been shown that liquid solutions of potassium tri-iodide can be used for the preparation of polyiodo-derivatives[107], but there is a risk of a side reaction involving protolysis, as a result of which the iodo-derivatives obtained are sometimes contaminated and only mass spectrometry can serve as a criterion of their purity[86].

An alternative method of synthesis of polyiodoarenes[108] is based on the Jacobsen cross-reaction. In sulphuric acid, mono- or di-iodoarenes disproportionate with formation of polyiodoarenes. Since the initial iodo-derivatives can be readily obtained by one of the direct iodination methods described above, this reaction has acquired undoubted synthetic interest.

4. Decomposition of Organic Compounds of Polyvalent Iodine

It is known that the thermal decomposition of iodonium salts can be used as a preparative method of synthesis of aryl iodides (see, for example, Beringer et al.[109]). A similar method has been used successfully in the synthesis of *o*-iodobiphenyls, which are relatively difficult to obtain[110,111]. In 1966–67 Leffler and co-workers[112,113] showed that aryl iodosocarboxylates having the general formula $ArI(OCOR)_2$ are capable of undergoing thermal decomposition via a heterolytic mechanism with the intermediate formation of acyl hypoiodites, which are decarboxylated to the corresponding iodides:

$$ArI(OCOR)_2 \rightleftarrows \overset{\oplus}{ArI}OCOR\ \overset{\ominus}{RCOO} \rightarrow ArOCOR + (RCOOI) \xrightarrow{-CO_2} RI\ .$$

This reaction has been hardly investigated in its synthetic aspect, although phenyliodoso *o*-phenylbenzoate§ gives rise to *o*-iodobiphenyl in a moderate yield on thermolysis[114], while iodobenzene has been obtained in a low yield on photolysis of 2,4,6-trimethylphenyliodoso benzoate¶ in the presence of iodine[115].

The development of a simple and reliable method of synthesis of aryliodoso carboxylates+ [116] makes the preparation of aryl iodides by the decomposition of these compounds of potential synthetic value.

IV. THE MECHANISM OF THE IODINATION OF ARENES

Although the number of publications on the mechanism of the iodination of arenes is much smaller than that of the communications devoted to the investigation of the mechanism of chlorination or bromination, they are quite sufficient to reject the erroneous hypothesis, migrating from textbook to textbook (see, for example, Nesmeyanov and Nesmeyanov[117]), that "hydrogen iodide reduces the iodobenzene obtained". It is known that iodobenzene does not change on heating with hydrogen iodide and red phosphorus for 5 h at 182 °C.[118]

Another widely held erroneous view is that Lewis acids do not catalyse the iodination reaction. It has been shown[47] that copper(II) chloride is an effective catalyst of this reaction.

Direct iodination is an electrophilic aromatic substitution reaction; the iodination of benzoic acid involves the formation of *m*-iodobenzoic acid in 75–80% yield, while the iodination of toluene gives rise to a mixture of *o*- and *p*-iodotoluenes. Electron-donating substituents accelerate the reaction, while electron-accepting substituents retard it. In the presence of sulphuric and nitric acids, the substrate is iodinated and not nitrated; on the other hand, when benzene is treated with iodine and much greater amounts of sulphuric and nitric acids than required for monoiodination, *p*-iodonitrobenzene is produced[120]. Consequently, the compound is initially iodinated and then nitrated; in the reverse order of reactions, the main product would have been the *m*-isomer. Benzene iodinated in the presence of nitronium tetrafluoroborate also gives rise to iodobenzene. It has been suggested that the iodine cation, formed with participation of the nitronium cation in accordance with the scheme

$$2H_2SO_4 + HNO_3 \rightarrow NO_2^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}\ ,$$
$$I_2 + 2NO_2^{\oplus} \rightarrow 2I^{\oplus} + 2NO_2\ .$$

functions as the iodinating agent. However, this hypothesis must be treated with caution, since the existence of the iodine cation as a kinetically independent species is possible only in highly acid media (for an exhaustive review, see Arotsky and Symons[119]).

It has been suggested that the formation of acyl hypoiodite is a source of electrophilic iodine in many direct iodination reactions[46,55,56] (see above).

It has been found that the reactivity of toluene in the iodination reaction by the Tronov–Novikov method is 9.5 times higher than that of benzene[120]; under the same conditions, the relative rate of nitration of toluene compared with the nitration of benzene is 8.22.

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§(*o*-phenylbenzoato-*O*)phenyliodine (Ed.of Translation).

¶(Benzoato-*O*)-2,4,6-trimethylphenyliodine (Ed.of Translation).

+(Carboxylato-*O*)aryliodine derivatives (Ed.of Translation).

In the iodination reactions investigated, the constant ρ is negative and varies from −4.5 to −6.4; $\rho = -4.5$ for iodination in the presence of a mixture of sulphuric and nitric acids[120], $\rho = -6.27$ for electrochemical iodination[121], and $\rho = -6.4$ for iodination by the tri-iodine cation[122].

Bearing in mind the foregoing factors, iodic and periodic acids can be recommended as oxidants for the monoiodination of reactive substrates; particularly satisfactory results have been obtained in the iodination of alkylbenzenes by the Tronov–Novikov method. In order to introduce two iodine atoms into the aromatic ring, one may recommend iodination in the presence of phenyliodoso trifluoroacetate. Deactivated compounds are probably best iodinated by the Tronov–Novikov method or in the presence of silver sulphate; in the iodination by the former method, benzil is oxidised to iodobenzoic acid, while in the presence of silver sulphate it is successfully iodinated[123]. Satisfactory results have been obtained in many instances of the iodination of condensed aromatic hydrocarbons using iodic and periodic acids as oxidants, although the latter sometimes oxidises polynuclear aromatic compounds[124].

If it is necessary to obtain an iodo-derivative containing substituents in the molecule in positions which are difficult or even impossible to ensure by means of direct iodination, then the synthesis of aryliodides via organometallic compounds, particularly via organothallium compounds has to be recommended. In particular, the direct iodination of *p*-toluic acid in the presence of potassium permanganate leads to *m*-iodo-*p*-toluic acid (in 90% yield),[125] while the synthesis via an organothallium compound makes it possible to obtain *o*-iodo-*p*-toluic acid (in 75% yield);[93] whereas the direct iodination of azobenzene in the presence of phenyliodoso acetate leads to 4-iodoazobenzene (in an insignificant yield),[63] the synthesis via the organothallium compound makes it possible to obtain 2-iodoazobenzene (in 55% yield).[96]

Despite certain advances achieved in the synthesis of aryl iodides, the direct iodination of certain deactivated substrates, particularly six-membered nitrogen-containing aromatic heterocycles, remains problematical. New advances in direct iodination will probably be associated with the application of both new oxidants[125] and with the search for systems whereby hydrogen iodide can be removed from the reaction sphere by another procedure[126,127].

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Lenin Komsomol (Young Communists' League)
Tomsk State Pedagogic Institute

Translated from *Uspekhi Khimii*, 53, 595-624 (1984) U.D.C. 541.67:547.1.118

Intramolecular Electronic Interactions in Phosphorus Compounds in the Light of Recent Structural Studies

R.P.Arshinova

The nature and mechanism of intramolecular electronic interactions in compounds of three- and four-coordinate phosphorus have been critically examined on the basis of a review of the results of the study of their three-dimensional structure and physical properties. The high π-acceptor power of phosphorus-containing groups, capable of stabilising conformations with the *trans*-orientation of the interacting orbitals of the donors (the *n*-orbitals of the unshared electron pairs of the heteroatoms or the π-orbitals of unsaturated systems) and the acceptors (bonds of the phosphorus atom) has been proved.
The bibliography contains 193 references.

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I. INTRODUCTION

The development of the theory of intramolecular electronic interactions is related to the experimental and theoretical analysis of more complex hetero-organic compounds, among which a leading place is occupied by organophosphorus compounds (OPC). The exceptional ability of the phosphorus atom to take part in electronic interactions of the most varied types, due primarily to the possibility of a change in the coordination number of this atom from one to six, is well known. The presence of unoccupied orbitals and unshared electron pairs (UEP), the high polarisability and polarity of the bonds formed by phosphorus, and the ability to form donor–acceptor and multiple bonds make it possible to construct any required model of OPC for the study of intramolecular electronic interactions.

An important contribution to the solution of the problem of the nature of electronic effects has been made by the concepts of three-dimensional structure. The combined study of the three-dimensional and electronic structure makes it possible to formulate fundamentally new, deeper, and comprehensive ideas on the nature, mechanism, location, and spatial-directed character of intramolecular electronic interactions. For organic compounds, these ideas have made it possible to approach an understanding of general regular features, and an elegant and systematic structural theory has been developed[1,2], in which the qualitative model of a one-electron molecular orbital has been used as the theoretical basis for discussing most problems. This approach makes it possible to develop a general theory of three-dimensional structure and chemical reactivity.

The development of the quantum-mechanical theory of conformational analysis has led to the introduction of the following types of intramolecular electronic interactions, not dealt with in the classical theory of electronic displacements: 1) the π- and σ-interactions of non-bonded atoms; 2) π- and σ-conjugation interactions; 3) geminal interactions; and 4) the effects of the ionic character of bonds. In the opinion of Epiotis and co-workers[1], these interactions form an "alphabet" for predicting the characteristic structural features of organic compounds, and to a considerable extent make it possible to model systems with a required geometry. A monograph by Epiotis[2] clearly defines the three-dimensional and geometric restrictions and various physical characteristics (displacement of electron density, ionisation potentials, etc.) indicating the existence of different types of electronic interaction. This makes possible the further development of the theory as applied to more complex hetero-organic compounds on the basis of available factual material.

The electronic structure of OPC and the effects of the mutual influence of atoms which they show have been the subject of many studies. Most of them were carried out in the nineteen-sixties from the viewpoint of the "*d* orbital concept",[4,5] which has often been criticised[6], so that up to the present, the problem of the participation of the *d* orbitals of the atoms of non-transition elements in chemical bond formation has not been resolved. The approach in the form of a correlation analysis has been fairly widely developed[7–9]. Overall, however, an urgent need has grown for a systematic analysis of intramolecular electronic interactions in OPC on the basis of present-day views on the nature and mechanism of electronic interactions. The foundation for this approach should be provided by the extensive factual data on the conformational behaviour of OPC and their physical properties. The results of the conformational analysis of OPC have been summarised in a number of reviews[10–12]. Extensive additional information on the geometric parameters, the nature of electron displacements, and the energy characteristics of boundary orbitals is provided by various physical methods. Many of these results (electron and X-ray diffraction, NMR spectroscopy) are given in reviews of the conformational analysis of OPC,[10–12] and others are given in reviews of the use of photoelectron spectroscopy[13–15], dipole moments, and the Kerr effect[16,17] in the chemistry of OPC; an appreciable proportion of the results have been published in the past five years only in original papers.

The present review examines from this viewpoint the compounds of three- and four-coordinate phosphorus [P(III) and P(IV)] in order to detect and identify intramolecular electronic interactions. The important role played by the electronic nature and structure of reagents in determining a preferred reaction path (including OPC [18]) is well known, so that the development of present-day views on the mecha-

nism of the mutual influence in OPC should stimulate the interest of chemists in revealing the fundamental relationship between three-dimensional structure, electronic structure, and the chemical reactivity of hetero-organic compounds.

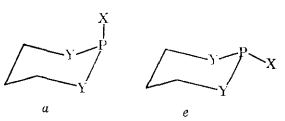
II. ELECTRONIC INTERACTIONS OF TERVALENT PHOSPHORUS WITH *n*-ELECTRON-DONOR SUBSTITUENTS

The directed study of various properties of cyclic P(III) compounds in the last ten years has provided a basis for a deep analysis of the effects of the mutual influence of atoms in the systems studied. The most comprehensive and complete studies by various physical methods have been carried out for 2-X-1,3,2-diheterophosphorinanes. The following brief review of studies carried out in this field will be restricted to an examination of the most fundamental characteristics of the molecule in order to investigate the nature and mechanism of intramolecular electronic interactions.

1. THE MANIFESTATION OF INTERACTION IN EXPERIMENTAL CHARACTERISTICS

a) Three-dimensional Structure

The most complete and extensive conformational studies have been carried out for 2-X-1,3,2-diheterophosphorinanes. The results have been summarised in a number of reviews[10-12, 19,20]. The conformations of cyclic systems with a P atom in the ring are determined by the nature of its intracyclic substituents. If this is a heteroatom (Y = NR, O, S), the chair form with the exocyclic bond in the axial (*a*) position predominates.



a *e*

An exception was found for the dialkylamino-group (X = NR_2, Y = O).[21-27] The observed deviations are due chiefly to steric interactions. The replacement of the heteroatoms by carbon atoms leads to a decrease in the energetic preference for the *a*-form, the proportion of which increases when heteroatoms with a small volume are introduced in positions 3 and 5 relative to the phosphorus atom. This clearly defined trend towards the stabilisation of one form, which is unfavourable in the light of steric repulsion effects (for cyclohexane derivatives, the *e*-conformation is preferred) indicates the strictly stereospecific nature of the effect, leading to an energy gain in favour of the *a*-orientation of the exocyclic substituent.

b) Electron Density Distribution

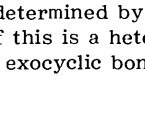
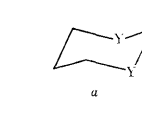
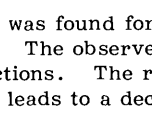
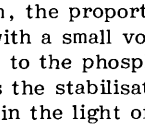
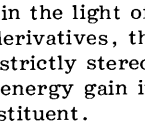
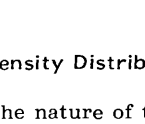
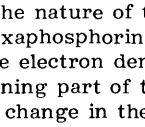
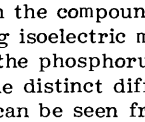
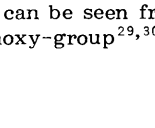
Change in the nature of the exocyclic substituent X in 2-X-1,3,2-dioxaphosphorinanes (Y = O) leads to consideragle changes in the electron density distribution in the phosphorus-containing part of the molecule. Quantitative information on the change in the polarity of the bonds formed by phosphorus in the compounds being considered has been obtained using isoelectric maps (Table 1).[16] These data indicate that the phosphorus bonds have a high electron mobility. The distinct differences in the properties of the substituents can be seen from Table 1: the chlorine atom[28] and the phenoxy-group[29,30] have acceptor properties, leading to the transfer of electron density from the ring oxygen and phosphorus atoms towards the substituent X; the dialkylamino-group is a UEP donor, and the migration of electron density takes place in the opposite direction, towards the ring oxygen atoms[27]. In 2-ethoxy- [16,29] and 2-phenyl-1,3,2-dioxaphosphorinanes[31], the nature of the electron density distribution differs little from that in the symmetrically substituted compounds[16], although the first compound shows slight non-equivalence of the P–O bonds. The increase in the polarity of the P–Cl bond in the ring compared with PCl_3 corresponds to a decrease in the frequency of the ^{35}Cl NQR signal (20.19 MHz compared with 26.208 MHz for PCl_3).[32]

Table 1. Dipole moments of the phosphorus bonds in 2-X-1,3,2-dioxaphosphorinanes and compounds PX_3.

Group	*m*, D	Substituent X				
		O (Ph) [30]	Cl [28]	O [R] [16, 29]	Ph [31]	N (R)$_2$ [27]
O_2PX	m_{P-O}	−0.8	−0.72	−0.32	−0.06	0.65
O_2PX	m_{P-X}	0.22	0.92	0.14	−0.95	0.37
PX_3	m_{P-X}	0	0.56	0	−1.18	−0.25

Note. Numbers in square brackets denote references (Ed. of Translation).

Table 2. Experimental parameters of cyclic systems with a P–Cl bond.

No.	Compound	ν, MHz [32]	l_{P-Cl}, Å [34]	γ_{P-Cl}, Å^3 [16]
(I)		15.797	2.190	—
(II)		17.08	—	—
(III)		17.6	2.174	—
(IV)		18.64	—	—
(V)		19.86	2.105	0.34
(VI)		20.19	2.128	−0.67
(VII)		21.55 22.19	—	—
(VIII)		24.524	2.153 [35]	—
(IX)		25.79	—	−1.33
(X)	PCl_3	26.208	2.043	2.66

Notes: ν is the frequency of the signal in the ^{35}Cl NQR spectrum, l_{P-Cl} is the P–Cl bond length, and γ_{P-Cl} is the anisotropy of the polarisability of the P–Cl bond.

Note. Numbers in square brackets denote references (Ed. of Translation).

The frequency of the ^{35}Cl NQR signal, which reflects the shielding of the chlorine atom, is used to estimate the polarity of different bonds formed by the chlorine atom[33].

The ^{35}Cl NQR spectra of 2-X-1,3,2-diheterophosphorinanes have been studied[34]. The experimental data obtained (Table 2) make it possible to follow the change in the dipole moment of the P–Cl bond (m_{P-Cl}) with change in the nature of the substituent Y in the fragment Y_2PCl; the frequency decreases considerably (from 26.208 MHz to 17.08 MHz), so that the dipole moment increases in the following order of substituents: Cl > S > O > NR. On going from five- to six-membered rings, the frequency increases by approximately 1 MHz. The greatest displacement of electron density to the chlorine atom is observed for the 1,3,2-diaza-derivatives.

c) Bond Polarisability

The anisotropy of the bond polarisability (γ) is one of the most sensitive characteristics of different types of intramolecular electronic interaction. 2-X-1,3,2-dioxaphosphorinanes show extensive changes in the anisotropy of the polarisability of the P–O and P–X bonds, compared with the corresponding symmetrically substituted compounds[16] (Table 3). With increase in the acceptor properties of the substituent X in 2-phenoxy-[30] and 2-chloro-1,3,2-dioxaphosphorinanes[28] there is an increase in the longitudinal component of the polarisability ellipsoid of the P–O bonds. In the chloro-anhydride (VI) there is a marked increase in the perpendicular component of the polarisability ellipsoid of the P–Cl bond b_T and a corresponding decrease in γ ($\gamma = -0.67$ Å^3), compared with PCl_3 ($\gamma = 2.66$ Å^3).[28] An even greater increase in b_T is observed for 2-chloro-1,3,2-dithiaphosphorinane (IX) (see Table 2).[38] In the chlorophosphite series, the changes in γ for the P–O and P–Cl bonds of the O_2PCl group are inversely proportional: decrease in the longitudinal component for the P–Cl bond is accompanied by an increase in the longitudinal component for the P–O bond[16].

Table 3. Anisotropy of the polarisability of the phosphorus bonds in 2-X-1,3,2-dioxaphosphorinanes and in compounds PX_3.

Group	γ, Å^3	Substituent X			
		Cl [28]	O (Ph) [30]	C_{sp^2} (Ph) [36]	N (Me_2) [37]
O_2PX	γ_{P-O}	3.27	3.11	1.95	2.12
O_2PX	γ_{P-X}	−0.67	2.35	4.0	2.24
PX_3	γ_{P-X}	2.66	−0.59	--	2.81

Note. Numbers in square brackets denote references (Ed. of Translation).

d) Bond Lengths

The data obtained up to the present on the P–Cl bond lengths in various 2-X-1,3,2-diheterophosphorinanes and their five-membered analogues (Table 2) show wide changes in the P–Cl values in a range of 0.15 Å [from 2.043 Å in compound (X) to 2.190 Å in compound (I)]. The P–Cl bond length increases on going from PCl_3 to the dioxa-derivatives and then to the dithia- and on to the diaza-derivatives, which show the greatest increase in the antibonding character of this bond. A functional relationship has been established between the values of the anisotropy of the polarisability γ and the bond length l.[16,38] The bonding increases with increase in the positive contribution to γ. The greatest increase in the transverse component of the P–Cl bond, that is the greatest increase in the antibonding character of the bond, is to be expected in the oxaza- and diaza-derivatives of the chloro-anhydrides of acids of tervalent phosphorus.

e) Valence Angles

An interesting characteristic of the geometric structure of 2-X-1,3,2-diheterophosphorinanes with a P–X bond in the α-position, and of many acyclic P(III) compounds, is the increase in the valence angles at a heteroatom (O, N) adjoining the P atom, and there is a clearly defined trend towards the sp^2 hybrid state of the heteroatom. The intracyclic angle at the oxygen atom is close to 120° in 2-chloro-1,3,2-dioxaphosphorinane[39] and 5-spiro-2-methoxy-1,3,2-dioxaphosphorinane[40]. The sum of the angles at the nitrogen atom in 1,3,2-oxaza-[41,42] and diazaphospholans[43] and in amidophosphites[44–47] is close to 360°. According to Dewar's calculations[48], the planar form for the nitrogen atom becomes energetically favourable only when the conjugation energy $\delta E_\pi \geq 18$ kcal mole^{-1}. This condition is not satisfied even for aniline and amides. The flattening of the pyramid of a nitrogen atom situated next to phosphorus has been discussed many times[49], but no satisfactory explanation has yet been found; it is clear only that a non-standard sp^2 electronic state of the heteroatoms indicates considerable interactions with the "liberated" p unshared electron pair of the heteroatom.

f) Energies of the Highest Occupied Molecular Orbital (HOMO)

The interpretation of photoelectron spectra in the approximation of Koopmans' theorem makes it possible to estimate the orbital energies, which are equated to the ionisation potentials. Studies of this kind have been carried out for 2-X-1,3,2-dioxaphosphorinanes with X = NMe_2, OMe, Cl;[50,51] the ionisation energies of the HOMO n_P, n_N, and n_O have been obtained. There is no splitting of the orbitals of the unshared electron pairs (UEP) of the nitrogen and phosphorus atoms in the 2-dimethylamino-derivative. The ionisation potential of the orbital n_P does not obey the additivity rule, because of the interaction of the UEP of the phosphorus atom with the UEP of the adjacent heteroatoms: $n_O - n_P$, $n_N - n_P$, $n_{Cl} - n_P$. The ionisation potentials of the UEP of the oxygen atoms undergo smaller changes; the n_O orbital in the dimethylamino-derivative is destabilised to a much greater extent (10.0 eV), compared with chlorophosphite (10.76 eV). Overall, the cyclic compounds show an increase in the same sense in the energies of all the highest occupied molecular orbitals, and this can be attributed to the difference in the direction of the $n-\sigma^*$ hyperconjugation interaction.

2. THEORETICAL INTERPRETATION OF EXPERIMENTAL DATA

All the above factors prove the high electron lability of the Y_2PX group. The observed electronic effect (or set of effects) is strictly stereospecific, and leads to stabilisation of the α-orientation of the polar bond P–X in the 2-X-1,3,2-diheterophosphorinanes. In all cases the phosphorus atom is adjacent to a heteroatom whose electronic state, according to data on the valence angles, is close to sp^2 hybridisation, so that the heteroatom acts as a p_π-UEP donor. The phosphorus atom, together with the adjoining bonds, shows

clearly defined π-electron-acceptor properties. The π-electron-acceptor effect is apparently not particular but universal in character, and is the main reason for the marked difference between the properties of the compounds of the elements in period II and subsequent periods. This problem was recently examined for compounds of silicon[52,53], arsenic[54,55], sulphur, and phosphorus[55,56]. The problem is of considerable importance for an understanding of the characteristic features of the chemical behaviour of heteroorganic compounds of the non-transition elements as a whole.

There arises the question of whether the high electron lability of P(III) compounds can be interpreted on the basis of existing ideas on intramolecular electronic interactions.

a) $d_{\pi}-p_{\pi}$ Interaction

The traditional explanation of the π-electron-acceptor properties of the phosphorus atom is related to the presence of its unoccupied 3*d* orbitals[4,5]. It is considered that $d_{\pi}-p_{\pi}$ conjugation leads to an increase in the strength of the bonding between the phosphorus atom acting as acceptor and the neighbouring heteroatom acting as donor. For 2-X-1,3,2-diheterophosphorinanes, the participation of the *d* orbitals of the phosphorus atom should have led to only an increase in the double-bond character of the bonds. In fact, however, as noted above, an increase in the antibonding character of the exocyclic P–Cl bond is observed. Even in those cases where the intracyclic substituents Y have a higher electronegativity (Y = NR, O) than the chlorine atoms in PCl_3 (which undoubtedly should have led to the participation of the d_{π} orbitals in bonding as a result of the increase in the positive charge on the central atom), the P–Cl bond is destabilised, compared with the same bond in PCl_3. Analysis of the direction of the displacement of electron density also indicates that the participation of 3*d* orbitals is unlikely. For $d_{\pi}-p_{\pi}$ conjugation, the displacement of electron density should take place towards the P atom; it follows from the data in Table 1, however, that for each case it is possible to show examples of the opposite direction of the effect (in 2-dialkylamino-1,3,2-dioxaphosphorinanes, the electron density is displaced towards the ring oxygen atoms). Moreover, the material obtained indicates that the effect is not localised on the central atom, and the electron acceptor in all cases is the neighbouring bond (the P–Cl bond in 2-chloro-1,3,2-diheterophosphorinanes).

Thus the increase in the antibonding character of the acceptor bond, the direction of the displacement of the electronic charge, and the extension of the transfer of electron density beyond the phosphorus atom towards the acceptor bond cast doubt on the possibility of interpreting the effect on the basis of the concept of $d_{\pi}-p_{\pi}$ conjugation.

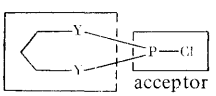
b) Electrostatic Geminal Interaction

Significant (analogous in strength and direction) effects of electron density displacement have been observed for organic compounds of the elements of Group IVb (E = Si, Ge, Sn) containing the group X–C(Cl)–E (X = Hal, O, N, S).[53] The magnitude of the interaction, as in the case of 2-X-1,3,2-diheterophosphorinanes, does not correspond to the electronegativity of the atoms and the inductive effect of the substituents. This effect has been called the geminal interaction of atoms or the α-effect+.[53] Systematic studies of the ^{35}Cl NQR spectra of compounds containing the Cl–C(Cl)–Si group led Feshin and co-workers[53] to conclude that the anomalous properties of the compounds are due to the electrostatic interaction of the charge of the atom E with the electron cloud of the C–X bond. The hypothesis of a possible electrostatic interaction by a field effect mechanism was verified for compound (VI).[59] Calculation showed that the dipole moment of the P–Cl bond should increase by 0.23 D. Under the influence of the electric field of the P–Cl dipole [0.56 D in compound (X) or 0.92 D in compound (VI), see Table 1], electron density is displaced from oxygen to phosphorus, and the dipole moment changes by 0.12 D or 0.17 D respectively. According to the isoelectric maps, however, the moment of the P–O bond increases by 0.72 D on going from the symmetrically substituted phosphites to compound (VI).[28] Thus electrostatic interactions, although acting in the appropriate direction, cannot fully explain the extensive changes in electron density taking place.

c) $n-\sigma^*$ Hyperconjugation Interaction

The stabilisation of the *a*-orientation of a polar substituent in 1,3,2-diheterophosphorinanes lies within the framework of the anomeric effect, the nature of which has been discussed many times[60] and is now related to the interaction between the *p*-type UEP of the ring heteroatom and the antibonding MO of the exocyclic polar bond. Moreover, the increase in the polarity of the P–Cl bond, the increase in its length, and the decrease in the frequency of the ^{35}Cl NQR signal, observed for 2-chloro-1,3,2-dioxaphosphorinane, correspond to the variations in these parameters in α-chloroethers containing the Cl–C–O group.[1,61–65] The anomalous behaviour of α-chloroethers has been widely studied, and has been called the α-effect,[61] the mechanism of which (the interaction of the *p* orbital of the UEP of the oxygen atom with the antibonding orbital of the C–Cl bond $n_O-\sigma^*_{C-Cl}$[61–65] is analogous to that of the anomeric effect. The possible existence of this interaction is 2-X-1,3,2-diheterophosphorinanes has also been examined in detail[59].

In 2-chloro-derivatives (XI), two fragments are clearly distinguished: an electron-acceptor fragment with a P–Cl bond, and an electron-donor fragment with 1,3-heteroatoms Y;[39–43,47] the best electron donor is a semi-localised orbital of the *n**-type formed by the reaction of two equivalent *p* orbitals of the UEP of the heteroatoms Y.[66,67]



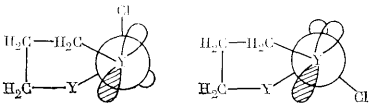
(XI)

According to the values of the ionisation potentials of the orbitals of the UEP of the atoms in OPC,[15] the donor power decreases in the following order: $n_N > n_S > n_P > n_O > n_{Cl}$; the increase in the π-electron-donor power of the sulphur atom compared with the oxygen atom is attributed to the fact that it adjoins the low-lying unoccupied molecular orbital (LUMO) (σ^*_{P-Cl}).[68]

+The term "α-effect" has another meaning[57,58], which is used later in the present review (Russian page 603). To avoid ambiguity in terminology, and following Feshin and co-workers[53], the effect being discussed here will be called the effect of the geminal interaction of the atoms.

The acceptor power of bonds is also closely related to their ionisation potentials[1,15]; it increases on going to bonds formed by elements of period III. Unfortunately, data on the ionisation potentials of the phosphorus bonds are not so unambiguous as the values of the ionisation potentials of the higher-lying orbitals of the UEP.

The donor and acceptor fragments of the molecules of 2-X-1,3,2-diheterophosphorinanes interact with one another in different ways in the two alternative conformations with *a* and *e* P–Cl bonds.



a—P—Cl; (T) *e*—P—Cl; (G)

The *e* position of the P–Cl bond is characterised by the gauche orientation (G) of *n* and the P–Cl bond, and the axial position by the *trans*-orientation (T). The $n-\sigma^*$ interaction is a maximum for the T-orientation of the orbitals being considered[1]. This interaction leads to considerable stabilisation of the T conformer, and indicates that there is transfer of the charge of the *p*-UEP of the Y atoms to the P–Cl bond; this also leads to an increase in the charge on the chlorine atom and a decrease in the charge on the ring Y atoms. The greatest effect of electron density transfer is observed for 2-chloro-1,3,2-diazaphosphorinanes (the frequency of the ^{35}Cl NQR signal is a minimum), since the nitrogen atoms are better electron donors than the oxygen and sulphur atoms. The sulphur atoms in turn are characterised by stronger donor properties than the oxygen atom. This explains why the length of the P–Cl bond and the anisotropy of its polarisability have intermediate values, compared with the dioxa- and diaza-derivatives. According to the ^{35}Cl NQR frequencies, however, the transfer of electron density is slight; this is related to the diffuse character of the UEP of the sulphur atom compared with the 2*p* orbitals of the UEP of oxygen and nitrogen. The latter are not diffuse, the charge of the two electrons is concentrated in a small region, and for them the $n-\sigma^*$ conjugation is reflected in the form of the charge transfer.

The interaction should also lead to an increase in the length of the acceptor bond[1]; the bond formed by the donor atom, however, may become stronger (a decrease in the length of the C–O bond in α-chloroethers is observed[65,69]). In 2-chloro-1,3,2-diheterophosphorinanes, the P–Cl bond in fact becomes longer, the increase being greater, the greater the donor power of the heteroatoms Y (in the order O < S < N).

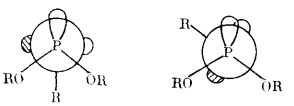
Change in the nature of the substituent X (in the P–X bond) should be reflected in the magnitude of the $n-\sigma^*$ interaction. The ionisation potentials of the bonds P–O(R) and P–C are approximately the same, and their absolute values are greater than those for the P–Cl bond[15,67], so that for the corresponding compounds the interactions are less clearly defined.

d) The α-Effect and the Acceptor Power of Bonds

Comparison of the above data for OPC and published data data[1,61–65] for α-chloroethers indicates that the effect of $n-\sigma^*$ hyperconjugation interaction in OPC is much greater. Calculations show that a position next to a low-lying unoccupied molecular orbital leads to an increase in the π-electron-donor power of heteroatoms[68]. In the present section, the factors leading to an increase in the acceptor power of bonds are examined. This increase is due to the decrease in the energy of the σ^* orbital, which is to a large extent related to the destabilisation of the acceptor bond. In the case of the P–Cl bond, the increase in the antibonding character is due to the familiar α-effect, typical of systems containing adjacent UEP.[3,57,58] The effect itself is often related to the stabilisation of the transition state[57], so that until recently, its influence on the physical properties was not examined. According to quantum-mechanical calculations[58], however, the α-effect is characterised formally by the destabilisation of the ground state, due to the interaction of the UEP of adjacent heteroatoms. Often (but not always), conditions are created for an antisymmetric combination of UEP, which leads to a more diffuse distribution of the electron density of the occupied molecular orbital with a nodal plane and perpendicular to the line of the bond; in the opinion of Bentrude and Tan[23], this should lead to a high "non-uniformity" of the polarisability of the bonds.

In this respect, the P–Cl bond is apparently one of the best acceptors; it has a high polarisability $b = 10.04$ Å^3,[16] due to the diffuse distribution of the electron density. Moreover, the destabilising repulsion of the n_P-n_{Cl} orbitals is appreciable for all orientations of the n_P orbital. In most other cases, however, the molecule can avoid unfavourable interactions of adjacent UEP by conformational rearrangements.

For other bonds formed by phosphorus, in which it is next to elements of groups V and VI b, the presence or absence of the α-effect depends on the conformational characteristics. In 2-alkoxy-1,3,2-dioxaphosphorinanes, the P–O bonds differ in their rotational-isomer properties: for steric reasons, the exocyclic bond cannot achieve the T-conformation characteristic of the ring bonds, and it has the G-orientation[29]



$n_O \perp n_P$; (T) $n_O \parallel n_P$; (G)

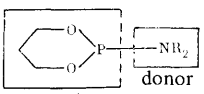
In the G-conformation, the repulsion between the UEP of the oxygen and phosphorus atoms n_O-n_P is a maximum. This conclusion is confirmed by an analysis of the photoelectron spectra. Studies of a whole series of trialkyl phosphites, in which there is a gradual change from GGG structures to structures with the T-orientation of all three alkoxy-groups[50,51], show that the n_O-n_P interaction is a maximum in the G-conformation, and can be estimated (by means of the parameter β_{OP}^{π}) as 0.58 eV. The interaction between the UEP of the oxygen and phosphorus atoms is so great that it leads to extensive variation in the ionisation potential of the orbital n_P (of the order of 1 eV), depending on the rotational-isomer properties of the P–O bonds.

Thus P–O bonds which are non-equivalent according to their conformational characteristics also differ in their energy parameters; the antibonding character of the exocyclic bond increases considerably, and it acts as the acceptor of the UEP of the ring oxygen atoms. The effect is reflected in the relative increase in the length of the exocyclic P–O bond, compared with the ring bonds (1.626 and 1.616, 1.611 Å according to X-ray diffraction data for 3,9-dimethoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane[40]), and also in the displacement of electron density, detected from the isoelectric maps, from the ring oxygen atoms towards the exocyclic P–O bond[16].

In 2-alkylamino-1,3,2-dioxaphosphorinanes, the α-effect of n_N-n_P repulsion is not detected by photoelectron spectroscopy[50,51]. The absence of splitting of the n_N and n_P orbitals shows that the interaction between them is slight, so that they are oriented at right angles to one another.

e) The Exo-anomeric Effect

The exo-anomeric effect was introduced[70] to explain the stabilisation of the structures with *e* C–O bonds in 2-alkoxytetrahydropyrans. In 2-X-1,3,2-diheterophosphorinanes, the *e* conformation is typical of compounds (XII) (X = NR_2 [10,27])



(XII)

In this compound, the best donor (the dialkylamino-group) is removed beyond the ring[39]. The orbital of the UEP of the nitrogen atom, situated next to P(III), has a comparatively low ionisation potential of 8.65 eV [for compound (XII) with R = Me [51]]. This is 2 eV lower than the ionisation potential of the orbital n_O; thus the $n_N-\sigma^*_{P-O}$ interaction must be comparable in strength and of opposite direction, compared with the $n_O-\sigma^*_{P-Cl}$ interaction in compound (VI). This effect is in fact observed; the displacement of electron density takes place from the exocyclic nitrogen atom in the direction of the P–O bond (see Table 1).[27]

In the compounds being considered, there are optimum structural conditions for $n-\sigma^*$ interaction, in spite of the fact that the dialkylamino-group occupies the equatorial position, and not the axial position typical of all other types of X. For the *e* conformation, the P–O bonds have the GG′ structure, in which the α-effect of the destabilising repulsion of the n_O-n_P orbitals is a maximum, so that the acceptor properties of the bond increase. Since the dialkylamino-group is not fixed, the UEP of the nitrogen atom can always take the T-orientation with respect to the P–O bond, favourable for hyperconjugation interaction. For the *e* position of the dialkylamino-group this should be the so-called perpendicular conformation, in which the UEP of the nitrogen and phosphorus atoms are mutually perpendicular. This structure also follows from an analysis of photoelectron spectroscopic data[51].

The possibility of $n_N-\sigma^*_{P-O}$ interaction for the *a*-position of the P–N bond should be emphasised, but in this case it is difficult for the bulky dialkylamino-group to adopt the perpendicular conformation, favourable for $n-\sigma^*$ interaction. The *a*-conformation becomes the preferred conformation only when the bulky NR_2 group is replaced by less bulky groups: NHR (R = Alk, Ph) [26,71,72] or aziridyl,[26] NPh_2, pyrryl[73], or NCO[74], where the nitrogen atom has a planar structure. In this conformation, however, the acceptor power of the ring P–O bonds, which have the TT structure, is decreased, so that the energy of the $n_N-\sigma^*_{P-O}$ interaction is lower than that in compounds with an *e* P–N bond.

The *e*-conformation has also been established for 2-aminotetrahydrofuran[75]. To explain this, the authors cited introduce all possible types of orbital interaction, without distinguishing the predominant one [including interactions in exactly opposite directions, such as, for example, the interactions $n_O(\sigma\text{-type})-\sigma^*_{C-N}$ and $n_N-\sigma^*_{C-O}$]. The above experimental material for 2-alkylamino-1,3,2-dioxaphosphorinanes, together with an analysis of the characteristic stereochemical features of the bonds, make it possible to distinguish the key orbital interaction of the type $n_N-\sigma^*_{P-O}$.

Thus the combination of P(III) with different heteroatoms leads to a labile electronic system with a clearly defined ability to undergo electron-cloud rearrangement. This lability is due to related effects: the destabilising $n-n$ interaction (the α-effect), leading to an increase in the acceptor properties of the bonds; $n-\sigma^*$ hyperconjugation, strengthened by the α-effect; and the field effect. The magnitude of the displacement of the electron cloud of the UEP, the degree of antibonding character in the bond, and the rearrangement of its polarisability ellipsoid depend on the conformational parameters and on the position of the heteroatoms in the periodic system: the elements of period II are characterised by the transfer of the concentrated electron cloud of the 2*p* orbital of the UEP donor (which is responsible for the manifestation of the effect in changes in the dipole moments of the bonds and the ^{35}Cl NQR frequencies); the bonds of the elements of period III, as acceptor bonds, are more easily polarised, with an increase in their antibonding character, and this leads to an increase in their length and to an increase in the contribution of the perpendicular component of the polarisability tensor.

It should be noted that the observed intramolecular interactions are characteristic not only of cyclic compounds. Many of the above experimental observations for 2-X-1,3,2-diheterophosphorinanes are also observed for acyclic compounds[76,77]. The facts indicate that the effects of hyperconjugation interactions are also revealed to a considerable extent in P(IV) compounds[78].

The change from phosphorus compounds to the corresponding arsenic-containing compounds leads to an increase in the strength of the effect. The study of 2-chloro-,[79] 2-bromo-,[80] and 2-phenyl-1,3,2-dioxa-arsenanes[81] using isoelectric and isoanisotropic maps made possible a quantitative estimation of the degree of displacement of electron density and rearrangement of the bond polarisability ellipsoids. The results show that the observed orbital interactions are characteristic of a wide range of compounds, so that they must be taken into account in the interpretation of data on the physical and chemical properties of compounds.

III. CONJUGATION EFFECTS IN COMPOUNDS OF TERVALENT PHOSPHORUS WITH π-ELECTRON-DONOR SUBSTITUENTS

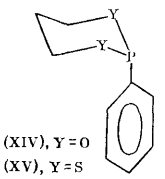
In organophosphorus compounds containing an unsaturated group next to a phosphorus atom, different types of conjugation are possible: $d-\pi$ conjugation, conjugation of the π-electrons of the unsaturated group with the UEP of the P(III) atom, and hyperconjugation of π-electrons with the vicinal bonds of the phosphorus atom. All these forms of intramolecular electronic interaction are strictly stereodirected, so that the study of the spatial characteristics of compounds to a large extent facilitates the identification of the predominant form of conjugation, determining the specific features of the physical and chemical properties of the compounds as a whole.

The monoaryl compounds of tervalent phosphorus $ArPX_2$ (XIII) can be considered, since they are less influenced by steric interactions than the diaryl and triaryl derivatives. The experimental study of these compounds has been carried out mainly in recent years.

1. THREE-DIMENSIONAL STRUCTURE

For monoarylphosphines (XIII) it is possible to have two three-dimensional structures, with parallel ($\omega = 0°$) or perpendicular ($\omega = 90°$) orientation of the UPE of the phosphorus atom (n_P) and the π-orbital of the benzene ring (Fig.1). Many compounds of this type have been studied by electron diffraction and the Kerr effect. An orientation of the *n*- and π-orbitals close to orthogonal has been

established for the following substituents: X = Cl (81°,[82] ~90° [83]); X = F (59° [84]); X = Alk (~90° [85]), X = CN (~90° [86]). The alternative conformation with $\omega \approx 0°$ has been found by infrared spectroscopy for the simplest compound of this series, phenylphosphine[86]. Relaxation NMR measurements have been used to determine the barriers to rotation of the PH_2 and PCl_2 groups (0.17–1.02 kcal mole^{-1} and 0.7 to 4.1 kcal mole^{-1} respectively) about the Ph–P bond[87,88]. Interesting results have been obtained for cyclic compounds with an exocyclic P–Ph bond (XIV) [36] and (XV).[38] In this case there is forced coplanar orientations of the n_P and π orbitals. Marked 1,3-synaxial interactions of the phenyl group in the α-position[31,36,38] rotate the benzene ring at an angle of 90° to the plane of symmetry of the molecule, which contains the UEP of the P(III) atom



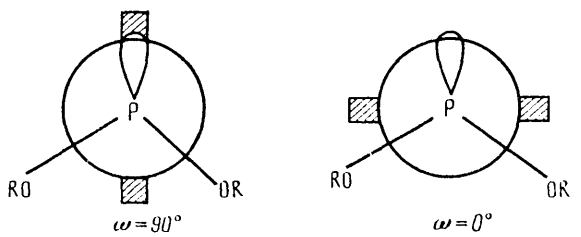


Figure 1. Boundary conformations of the benzene ring in arylphosphines.

The structure of the simplest monophenylphosphines has been studied many times by quantum-mechanical calculations. Non-empirical calculations in an STO-3G basis set for phenylphosphine and phenyldifluorophosphine (X = H, F) show that the UEP of the P(III) atom lies at right angles to the plane of the aromatic ring[89]; when the H, F atoms are replaced by Cl atoms, the alternative conformation (ω = 90°) becomes preferred[89]. Semi-empirical calculations have been carried out by MINDO/3 and MNDO methods with complete optimisation of the geometry of all potentially low-lying conformations[90]. Both methods, and also the CNDO/2 method[91,92], confirm the stabilisation of the structure with an almost parallel orientation of the n and π orbitals in phenylphosphine. The same methods indicate that phenyldimethylphosphine has an analogous structure[90]. For the dichloroderivative (MNDO method[93]), an orthogonal structure has been established, in agreement with the above experimental data.

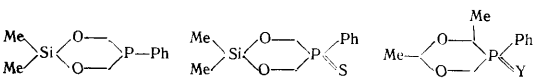
2. SPECTRAL STUDIES OF ELECTRONIC INTERACTIONS IN MONOARYLPHOSPHINES

Indirect information on structure, based on the analysis of the strength of the interaction between the phosphorus-containing substituent group and the π-electrons of the benzene ring, is provided by spectral methods. Most of the work on monoarylphosphines has been devoted to an analysis of the ultraviolet spectra.

The R-band in the range 230–260 nm is considered to be the most characteristic. It is due to the transfer of n_P to the benzene ring ($n \rightarrow \pi^*$ transition). Many authors assume that the intensity of the band is related to the relative orientation of the n and π orbitals. Evidence of the possible existence of this relationship is provided by the decrease in the intensity of the band on going from the cyclic 2,2-dimethyl-5-phenyl-1,3,2,5-dioxasilaphosphorinane (XVI) (9000 [94]) and the sterically unstrained compound (XIII) with X = Me (5550 [95,96]) to diethylphosphine (3920) and its dimesityl (1700) and di-t-butyl (1890) derivatives[95,96]. The decrease in the intensity of the R-band in phenyldialkylphosphines has been taken by many authors as proof that the compounds, in addition to the main conformer in which the n and π orbitals are orthogonal, also contain another conformer with geometry (ω = 0°) favourable for $n-\pi$ conjugation[95–97].

There are other viewpoints on the interpretation of the ultraviolet spectroscopic data. Some authors consider that when there is $p-\pi$ conjugation, the R-band should be absent, as observed for aniline derivatives[98–100]. It is suggested that the difference may be due to a difference between the energies of the orbitals of the UEP of the central atom and the π-orbitals of the benzene ring[101]; in aniline, the energy $E(n_N)$ is lower than $E(\pi)$, whereas in phenylphosphines (and phenylarsines), the order of the energies is the opposite [$E(n_P) > E(\pi)$], so that the $n \rightarrow \pi^*$ transition is observed in the ultraviolet spectra at long wavelengths.

The problem can apparently be solved by comparing the ultraviolet spectra of compounds whose three-dimensional structure has been studied. In the dialkyl phenylphosphonite series, the ultraviolet spectra have been characterised for the cyclic compound (XIV) with forced coplanar orientation of the n and π orbitals[101] and the acyclic diethyl phenylphosphonite $PhP(OEt)_2$ (XVII),[100] but there are no structural data for the latter. In the dialkylphenylphosphine R_2PPh series, no direct experimental results have been obtained on the structure of the cyclic analogue. Here, the ultraviolet spectra show an increase in the intensity of the R-band on going from the acyclic compounds ($\varepsilon \leq 5550$) to the cyclic compound (XVI) (ε = 9000).[94–96]



(XVI) (XVIII) (XIX), Y=O, S

The observed effect was attributed to the parallel orientation of the n_P and π orbitals in compound (XVI). A study of the three-dimensional structure of compound (XVI) using the Kerr effect did not make it possible to reach sufficiently definite conclusions about the orientation of the phenyl group[102]. Available data for the analogoues with P(IV) [for compounds (XVIII) [103] and (XIX) [104]], however, indicate a change in the conformation of α-Ph to the parallel conformation, compared with the corresponding 1,3,2-dioxaphosphorinanes, as a consequence of the fact that in these analogues there are no 1,3-synaxial interactions. In six-membered rings, the orientation of the plane of the benzene ring is determined primarily by steric effects[36], which are approximately the same in corresponding P(III) and P(IV) compounds. This indicates the need to obtain additional experimental data for systems of the 5-phenyl-1,3,5-dioxaphosphorinane type.

The above material on the structure and ultraviolet spectra show that it is as yet difficult to speak of the existence of a

direct relationship between the intensity and position of the *R*-band and the orientation of the *n* and π orbitals[101].

The electronic interactions in arylphosphines are analysed using the shielding parameters of the aromatic carbon atoms in ^{13}C NMR spectra[105-107]. The variation in these quantities on going from compounds (XIII) with X = H, Me to compounds with X = t-Bu is attributed[107,108] to conformational rearrangements; for compounds of the first type, in the opinion of the authors cited, there is free rotation of the phenyl group, whereas in the second case a conformation with orthogonal orientation of the *n* and π orbitals is produced.

The clearest picture of the magnitude and strength of the mesomeric interaction of a substituent X with a phenyl ring or an acetylenic bond can be obtained from the photoelectron spectra: the HOMO in phenylphosphines is formed by the interaction of the π-levels of benzene and the n_P orbital. The greater the splitting of the $b_1(n)$ and $b_1(\pi)$ orbitals from the photoelectron spectra, the greater the $n-\pi$ interaction. For compounds of the (XIII) series with X = Me,[100] X = Cl,[109] and X = OEt (XVII),[50,51] no significant splitting was detected. For phenylphosphine (X = H), the data obtained are not unambiguous[92,93,108-110], and they have been collected and examined with the introduction of data on other monophenylphosphines to refine the assignment of the bands in Ref.93; the splitting obtained (0.49 eV) indicates the existence of an interaction. It increases by a factor of 1.4 on going to t-butylethylphosphine[111]; for the corresponding chloro-derivatives, the splitting is much smaller[93,111].

An appreciable interaction of the phosphorus-containing group with the neighbouring π-electron system is indicated by an analysis of the photoelectron spectra of di-t-butylpheylphosphine and di-t-butylvinylphosphine[92]. The photoelectron spectra of the above compound (XVII), whose ultraviolet spectrum shows an *R*-band of medium intensity[100], have been discussed[50,51]. The second band in the spectrum of this compound is due to the ionisation of the π-electrons of the benzene ring. Its splitting into components corresponding to the orbitals $\pi(a_2)$ and $\pi(b_1)$ is slight, and is not recorded sufficiently clearly, but the components (9.22 eV and 9.40 eV) can be determined approximately[50,51]. The fact that the splitting of the π-orbitals is slight may indicate that their interaction with the UEP of the P(III) atom is slight. The experimental value of the ionisation potential of the n_P orbital obeys the additivity rule, and this is another indication that the mixing of the n_P and π orbitals is slight.

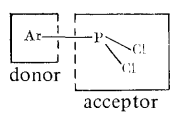
It follows from the above material on monophenylphosphines that the results obtained are often contradictory. The apparent reason is that the authors of almost all spectral studies assume that the π-orbitals of the benzene ring interact with the neighbouring fragment only in one form with ω = 0°, when $n-\pi$ conjugation is possible. An orbital examination (see next section) shows, however, that structural conditions are created for another form of conjugation, of the $\pi-\pi^*$ type, which undoubtedly also influences the position and character of the bands in the spectra (see for example Ref.92). Since spectral studies make it possible to reach conclusions only about the strength of the effects of conjugation with the π-orbitals of the benzene ring, it is obviously necessary to solve the problem of the manifestation of both types of conjugation in the spectral characteristics and their relation to the three-dimensional structure.

3. THE NATURE OF THE ELECTRONIC INTERACTIONS IN PHENYLPHOSPHINES

Drawing an analogy between the electronic structure of amines and phosphines with phenyl substituents, many authors at first assumed that compounds of tervalent phosphorus, like nitrogen compounds, should be stabilised by $p-\pi$ conjugation effects. Analysis of a large amount of experimental data and the electronic state of the P atom, however, led Tsvetkov and Kabachnik[112] to the conclusion that conjugation is inhibited in arylphosphines; these results led to extensive discussion[113]. In spite of this, in spectroscopic studies the results obtained are often interpreted from the viewpoint of possible $n-\pi$ conjugation; these studies have been criticised[114]. Overall, the structural data obtained[82-89], together with spectral characteristics[94-97], lead to the conclusion that there is limited $n-\pi$ interaction. A recent combined study[115] of the integral intensities of the bands due to the CH vibrations in the infrared spectra, the $^1J(C, H)$ spin–spin coupling constants, and the rate constants for deuterium exchange in the Me group in phenylphosphines showed the absence of $n-\pi$ conjugation.

In a paper[92] on the photoelectron spectra of vinyl- and phenylphosphines, it was suggested for the first time that the predominant form of electronic interactions in these systems is not $n-\pi$ or $d_\pi-p_\pi$ conjugation, nor an inductive effect, but $\pi-\sigma^*_{P-C}$ hyperconjugation. A similar conclusion was later reached[89] from an analysis of the values of the long-range spin–spin coupling constants $^5J(C, H)$ and $^5J(C, F)$ and the barriers to internal rotation in dihalogeno-derivatives of phenylphosphines[89]. Delocalisation of electron density in the direction from the phenyl group to P is detected from a comparison of the chemical shifts of the ^{13}C NMR signals of the benzene ring[116]. An analysis of the dipole moments of aryldichlorophosphines by a vector-statistical method[83,117] showed a significant displacement of the π-electron density of the aryl group towards the P–Cl bonds: the polarity of the $C_{Ar}-P$ bond decreases considerably on going from aryldichlorophosphines (1.43 D) to triarylphosphines (0.38 D [31]), arylphosphines (0.07 D [117]), and 2-phenyl-1,3,2-dioxaphosphorinane (0.25 D [31]); the dipole moment of the P–Cl bond increases to 1.87 D (compared with 0.56 D in PCl_3). The displacement of electron density from the aryl group to phosphorus cannot be explained within the framework of the concept of $n-\pi$ conjugation.

The dependence of the type of orbital interactions in aryldichlorophosphines on the spatial orientation of the aryl group can be considered. The molecule can be broken down into two fragments; the first, the aryl group, is a π-electron donor, and the second, as a result of the antisymmetric combination of unoccupied orbitals of the P–Cl bonds, forms a low-lying $\pi^*_{PCl_2}$ orbital (XX).



(XX)

With the parallel orientation of the n_P and π orbitals (see Fig.1, ω = 0°), steric conditions are created for $n-\pi$ conjugation, and with the perpendicular orientation (ω = 90°) for $\pi-\pi^*_{PCl_2}$ interaction[118]. For X = H, the energy of the orbital $\pi^*_{PH_2}$ is high, and $n-\pi$ interaction is more effective. The energy of the orbital $\pi^*_{PX_2}$ is lowered considerably when the H atom is replaced by Alk and more particularly by Cl, which leads to stabilisation of the bisector conformation. It should be noted that in vinylphosphines, interactions with the π-system should be more clearly defined, since in the phenyl compound they are weakened as a result of delocalisation of the π-electrons.

The analysis carried out makes it possible to explain the factual material which has now accumulated on the three-dimensional and electronic structure of arylphosphines. It shows that the increase in the π-acceptor properties of P-containing groups compared with their N-analogues radically alters the nature of the predominant form of electronic interaction, which, as in 2-X-1,3,2-dioxaphosphorinanes (see section II), is not limited to the phosphorus atom, but extends further towards the whole acceptor group.

In conclusion it should be noted that for arylarsines, electron diffraction distributions analogous to those observed for phosphorus compounds have been detected[117,119]; these can be fully explained within the framework of the concept of intramolecular electronic interactions discussed here.

IV. ORBITAL INTERACTIONS IN COMPOUNDS OF FOUR-COORDINATE PHOSPHORUS

The properties of P(IV) compounds of the type $X^1X^2X^3P{=}Y$ are to a large extent determined by the P=Y group, where Y = O, S, Se. The variation detected by different physical methods in various parameters of the P=Y bond with change in the nature of the substituent X [4,120,121] indicates that a significant role is played by electronic interactions with the P=Y bond. An analysis of the factors influencing such a fundamental characteristic of the bond as the electron density distribution must eventually make it possible to reach specific conclusions about its electronic structure. It is appropriate to follow from this viewpoint the influence of structural factors on the polarity m(P=Y) of the P=Y bond. Linear relationships have been established between the phosphoryl group wavenumbers in the infrared spectra and its dipole moment[122,123]. An attempt has been made to derive a relationship between m(P=Y) and the sum of the constants $\Sigma\sigma_i$ for Y = O, S, Se.[124] Recent detailed studies of the polarity[16,120,124,125], basic nature[126,127], and ionisation potentials[15] of heterophosphoryl bonds and the three-dimensional structure as a whole[10] are revealing a number of new relationships and the nature of the orbital interactions.

1. THE POLARITY OF THE P=Y BOND

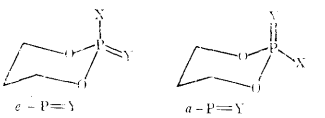
In symmetrically substituted compounds $X_3P{=}Y$, the polarity of the P=Y bond is estimated as the vector difference in the dipole moments of the P(III) and P(IV) compounds (for non-regular substituents X, rigidly fixed bicyclic structures are used).[16,125] Values have been obtained in this way for m(P=O), D:[16,37,125] C_3P (3.40) > N_3P (3.27) > Cl_3P (3.13) > O_3P (2.95); for m(P=S):[16,37,125] C_3P (3.88) > N_3P (3.19) > O_3P (2.62) > Cl_3P (2.03); and for m(P=Se):[124,128] C_3P (4.0) > N_3P (3.88) > O_3P (2.50). The observed increase in the range of variation in the values of m(P=Y) in the order Y = O, S, Se is apparently due to the increase in the polarisability of the P=Y bond (the total polarisability of the bond is b = 4.95 Å^3 for Y = O;[16] b = 13.64 Å^3 for Y = S;[16] and b = 17.63 Å^3 for Y = Se [129]). The effect is naturally more clearly defined for the easily polarised sulphur and selenium atoms.

The reasons for the change in the order of increase in the polarity of the P=Y bond in a series of compounds of the type $YP(OR)_3$; m(P=O) > m(P=S) > m(P=Se), and in the series of compounds YPR_3: m(P=O) < m(P=S) < m(P=Se), have been discussed[121]. According to photoelectron spectroscopic data, the formation of the P=Y bond is regarded as involving the σ-donor transfer of the UEP of the P(III) atom to an unoccupied orbital of the Y atom. The two unshared p-pairs of the Y atom are able to undergo a π-donor interaction of opposite sign with a molecular orbital of the PX_3 group, and this interaction is not limited to the central atom, and can extend in the direction of the atoms of the substituents X.[130]. Quantum-mechanical calculations by the CNDO/2 method also confirm the existence of a hyperconjugation interaction of degenerate orbitals n_Y with σ-bonding molecular orbitals of the P–X bonds[130]. In P(IV) compounds, the first ionisation potential corresponds mainly to the ionisation of the four p_π electrons of the Y atom, and it can serve as a measure of the back transfer of electron density[15]. For the compounds $X_3P{=}Y$ with Y = O, S, the ionisation potential decreases in the following order of substituents X_3:[15] Cl_3P > $(EtO)_3P$ > $(Me_2N)_3P$ > Me_3P. The polarity of the P=Y bond increases in the same order. This indicates the important role of delocalisation effects due to n–σ hyperconjugation interaction in the production of the electronic structure of the P=Y bond, and as in the case of tervalent P compounds, this effect is greatest for P–Cl and P–O bonds[121].

The donor power of the p_π orbital of the UEP of the atoms O, S, Se, according to their ionisation potentials[15], increase in the order O < S < Se. It is increased in the reaction with low-lying UEP of neighbouring atoms (X = OR, Cl) and is decreased in interactions with high-lying pairs (X = NR_2). Thus in compounds of the type $R_3P{=}Y$ in which the donor power of the UEP and the acceptor power of the P–C bonds are lowered, delocalisation effects are shown to the smallest extent; the order of the increase in m(P=Y) corresponds to the order of the polarisability of the donor–acceptor bonds: (P → O) < (P → S) < (P → Se).

The degree of back transfer of the four p_π electrons from the heteroatom Y is greater, on the one hand, for compounds with X = Cl and OR, and on the other hand for compounds with Y = Se, and then Y = S and Y = O. The superposition of the delocalisation effect also leads to a change in the order of the increase in the dipole moment of the P=Y bond in the compounds $(RO)_3P{=}Y$ and $R_3P{=}Y$.

The influence of the nature of the substituent X on the polarity of the P=Y bond is revealed in a study of unsymmetrically substituted compounds of the 2-X-2-Y-1,3,2-dioxaphosphorinane type (XXI).[121,125] It also depends on the conformational characteristics, as was first pointed out in a study of the dipole moments of 2-methyl- and 2,4-dimethyl-2-thiono-1,3,2-dioxaphosphorinanes[16]: the a and e P=Y bonds have different polarities[121].



The greatest difference was found for the compounds with X = H: for the a and e P=O bonds, the values obtained were 3.25 D and 2.95 D;[121,132] for X = NR_2 the differences are 0.25 D (3.60 D and 3.33 D for the P=O bond[133], and 3.53 D and 3.33 D for the P=S bond[134]). The smallest difference was observed for phosphonates (X = Me), where for the a and e bonds, m(P=O) is 3.36 D and 3.33 D.[126,135]

For conformationally uniform compounds, only the polarity of the e P=Y bond has been determined; it is a minimum in chlorophosphates (X = Cl) [m(P=O) = 2.40 D and m(P=S) = 2.10 D [125]]; in phosphates (X = OMe) it increases to 2.95 D and 2.68 D respectively[125]; and in the phenoxy derivatives (X = OPh) it is slightly greater than in compounds with X = OR.[136] The polarity of the P=Y bond has been estimated graphically in 2-phenyl-1,3,2-dioxaphosphorinane oxide and sulphide; the values found were 3.0–3.5 D and

2.8 D respectively[31]. Quantum-mechanical calculations have also detected variation in the polarity of the phosphoryl group with change in the nature of the substituent X in compound (XXI),[127] but the high absolute values obtained have been criticised[121]. Thus the dipole moments of the P=Y bonds in 1,3,2-dioxaphosphorinanes evidently undergo appreciable changes with change in the nature of X (in the range 1.0–1.5 D) and with change in the orientation of the P=Y bond (~0.3–0.5 D).

2. BASIC NATURE OF THE PHOSPHORYL GROUP

Changes in the polarity of the P=Y bond are reflected in the variation in the physical and chemical properties of the compounds. For the phosphoryl group, these characteristics are the vibrational wavenumbers in the infrared spectra and the basic character. The order of the basic nature of 2-oxo-1,3,2-dioxaphosphorinanes, determined relative to $\Delta\nu_{OH}$ for phenol[127], correlates with the magnitude of the dipole moment of the phosphoryl bond, and changes in the following sequence of X (Fig.2):[121]

$$Cl < OPh \sim H \sim OMe < Ph < Me < NR_2.$$

The order obtained also reflects the regular features found above: for electron-acceptor substituents, $m(P{=}Y)$ and the basic nature of the phosphoryl group are smaller than those for electron-donor substituents. Here, as in the symmetrically substituted compounds, the influence of delocalisation is apparently being shown. Unfortunately, data on the photoelectron spectra of 2-oxo-1,3,2-dioxaphosphorinanes are extremely limited (only the first ionisation potentials have been obtained),[137] so that a correlation with delocalisation effects is not possible[121].

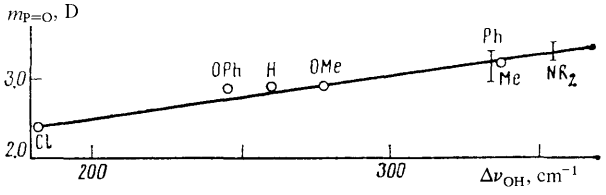
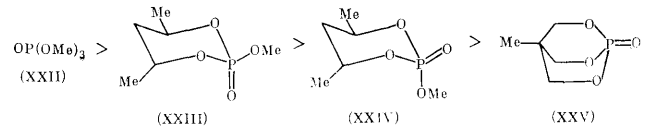


Figure 2. Correlation between the polarity and the order of basic nature of the phosphoryl group, determined relative to $\Delta\nu_{OH}$ for phenol[121].

In the discussion of the influence of the conformational characteristics on the basic nature and polarity of the P=Y bond, it is useful to compare the corresponding parameters of compounds with different three-dimensional structures and the same environment of the phosphorus atom. In 1,3,2-dioxaphosphorinanes, the more polar *a* P=Y bond should also be more basic. This order of basic nature of the phosphoryl oxygen atom was in fact established for the 2-hydro-2-oxo- and 2-methoxy-2-oxo-derivatives.[126] If however it is borne in mind that the *e*-orientation of the P=Y bond corresponds to the TT conformation of the P–O bonds, and the *a*-position to the GG′ conformation, it may be concluded that in the TT conformation, the degree of delocalisation of the p_π electrons of the Y atom is greater, and this leads to a decrease in the polarity of the P=Y bond[121].

An analogous relationship is revealed in the trialkyl phosphate series, for which the following order of decrease in the basic nature of the terminal oxygen atom was observed[126]:



The members of the series differ in their structural characteristics: for compound (XXII), the GGG conformation is preferred[138]; the second member of the series (XXIII) is characterised by equilibrium between the forms GGG ⇌ TGG′ (the conformation of the exocyclic group is given first);[139] the third member has the GTT conformation[139]; and the last member (XXV) has the TTT conformation[121]. As the T conformations accumulate, the effect of delocalisation increases, with a consequent decrease in the concentration of negative charge on the terminal oxygen atom and a corresponding decrease in its polarity and basic nature.

V. INFLUENCE OF PHOSPHORUS-CONTAINING GROUPS ON ELECTRONIC INTERACTIONS IN NEIGHBOURING FRAGMENTS (O-PHOSPHORYLATED PHENOLS)

Phosphorus-containing groups have such a marked ability to take part in different types of electronic interaction that they can also change the nature of the mutual influence of atoms in fragments adjoining them. An example is provided by O-phosphorylated phenols, for which a fairly large amount of factual material has been accumulated. They contain the fragment P–O–Ar. In organic compounds of this type, the anisoles R–O–Ar, $p-\pi$ conjugation between the oxygen atom and Ar predominates, leading to stabilisation of the conformations with the parallel arrangement of the *p* and π orbitals[140] and to transfer of electron density from the oxygen atom towards the benzene ring[141,142]. Extensive studies have also been carried out for anisoles in which, as a consequence of steric strain, inhibition of $p-\pi$ conjugation is observed[143–147], revealed by reversal of the sign of the dipole moment of the C_{sp^2}–O bond, which changes from −0.39 D in anisoles to 0.05 D in its sterically hindered analogues[144].

In O-phosphorylated phenols, the group joined to the Ar–O group is a strong competing π-electron acceptor, namely the phosphorus-containing group. The question of whether it is capable of inhibiting $p-\pi$ conjugation, and which of the effects is stronger, $p-\pi$ conjugation or π-electron-acceptor interaction, can be considered. The view is held that the introduction into anisoles of a second unsaturated group capable of conjugation does not inhibit conjugation, since it may involve both unshared *p*- and sp^2-pairs of electrons of the oxygen atom[142,148], whose energy difference is small[142]. Other data show, however, that the presence of two π-electron systems on an oxygen atom in the molecule of an organic compound weakens its conjugation with each system separately[141,143]. For the analogous silicon compounds, it is suggested that both UEP are involved in conjugation with the phenyl group and the group containing the heteroatom[52]. This interaction should lead to an appreciable decrease in the electron density on the oxygen atom. The competition between these two types of interaction facilitates the production of the one which is energetically more favourable. This should be reflected primarily in the three-dimensional structure of the compounds: for $p-\pi$ conjugation, the more favourable structure is that in which the plane of the benzene ring coincides with the plane of the C_{sp^2}–O–E bonds, and the *p* and π orbitals are coplanar (Fig.3, $\alpha = 0°$); in the alternative conformation, the planes being considered are

mutually orthogonal ($\alpha = 90°$), and the sp^2 orbital of the UEP is in the same plane as the phenyl π-electrons.

The available data on compounds containing the fragment Ar–O–P(III) or Ar–O–P(IV) can be considered in turn.

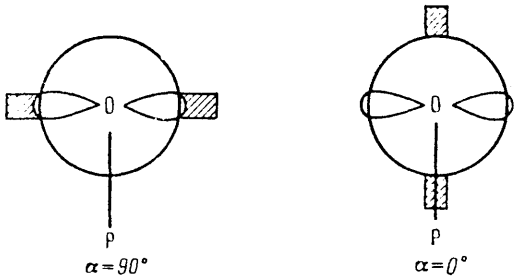


Figure 3. Boundary conformations of the benzene ring in O-phosphorylated phenols.

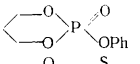
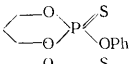
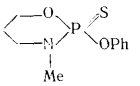
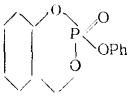
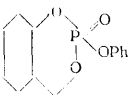
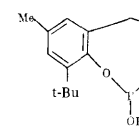
1. EXPERIMENTALLY MEASURED CHARACTERISTICS OF THE COMPOUNDS

a) Three-dimensional Structure of the Compounds

Within the framework of existing ideas, $p-\pi$ conjugation is energetically more favourable than $p_\pi-d_\pi$ conjugation, so that the production of conformations with parallel orientation of the p and π orbitals being considered is to be expected (Fig.3, $\alpha = 0°$). The results of most studies carried out up to the present, however, indicate the reverse: many types of phosphorus compound have a structure with an arrangement of the p orbital of the UEP and the π orbital of the benzene ring close to orthogonal (see later, Table 4). This orientation of the phenyl plane has been established by X-ray diffraction for phenoxythiophosphoryl hydrazide (XXXII), $\alpha = 87.2°$;[149] 2-phenoxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (XXVII), $\alpha = 84.2°$;[150] 1,8-naphthalene phenyl phosphite (XXXI) [151] and the eight-membered 2-phenoxy-4,5,7,8-dibenzo-6H-1,3,2-dioxaphosphocine (XXXIII), $\alpha = 75.5°$.[152] In solution, 1,3,2-dioxaphosphorinanes retain the conformation characteristic of the crystalline state[136]; an analogous structure is shown by the phosphoryl analogue[136] and aryloxy-derivatives of tervalent phosphorus compounds[30]. The orthogonal orientation has also been established for pyrocatechol aryl phosphites[153]. According to NMR data, phenyl dichlorophosphate also has an appreciably non-planar structure[154]. The introduction of substituents in the p-position of the benzene ring in 2-aryloxy-1,3,2-dioxaphosphorinanes does not influence the angle of rotation of the aryl plane, indicating indirectly the absence of conjugation.

The orthogonal orientation of the p and π orbitals found for O-phosphorylated phenols is possibly not the exception but the rule for compounds containing elements of period III next to an aryloxy fragment. Thus phenyl silyl ether[155] and trichloro- and trimethylphenoxysilanes[156] have a structure close to orthogonal, and sulphur compounds, namely the aryl esters of arylsulphonic acids, also show appreciable non-coplanarity ($\alpha \cong 90 \pm 20°$).[157]

Table 4. P–O and C_{sp^2}–O bond lengths in O-phosphorylated phenols.

No.	Compound	Position	Bond length, Å				Refs.
			P–O (Alk)	P–O (Ar)*	C–O (Alk)	C–O (Ar)	
(XXVI)		*a*	1.565	1.59	—	1.41	[163]
(XXVII)		*a*	1.575	1.594	—	1.410	[150]
(XXVIII)		*a*	1.576	1.605	—	—	[164]
(XXIX)		*a*	1.579	1.575 (r); 1.571 (e)	—	1.409	[165]
(XXX)		*a*	1.586	1.565	1.47	1.409	[166]
(XXXI)	$C_{10}H_6O_2POPh$	*a*	—	1.626 (r); 1.656 (e)	—	1.412	[154]
(XXXII)		*a*	—	1.642 (r); 1.618 (e)	—	1.408	[152]
(XXXIII)	Ph (CH_2O) P (S) $OC_6H_2Cl_2Br$	—	1.579	1.615	1.420	1.394	[167]
(XXXIV)	$(H_2N-NH)_2$ P (S)OPh	—	1.609	—	—	1.415	[139]
(XXXV)	MeOPh	—	—	—	1.423	1.361	[160]
(XXXVI)	*p*-$MeOC_6Me_4OMe$	—	—	—	1.47	1.38	[161]

*Here, r = ring, and e = exocyclic P–O bond.

b) Electron Density Distribution

To establish the mechanism of intramolecular electronic interactions, it is of value to analyse the polarity of the C_{sp^2}–O and P–O bonds of the Ph–O–P fragment. The high electronic lability of the C_{sp^2}–O bond in anisoles was noted above (range of change in the dipole moment from −0.39 D to 0.05 D [144]). Diphenyl ether also shows a reversal of the sign of the dipole moment of the bond compared with anisole; the moment is directed towards the oxygen atom[141]. The chemical shifts of the signals in the ^{13}C NMR spectra in various substituted phenols also confirm that variation in the polarity of the C_{sp^2}–O bond over a wide range, depending on the nature and position of the substituents in the benzene ring[158]. The polarity of the P–O bond also varies over a fairly wide range with change in the type of substituent on the phosphorus atom[16]. All these data indicate that the π-donor or π-acceptor transfer of electron density at the oxygen atom is reflected in the change in the dipole moments of the bonds.

Data have now been obtained on the polarity of the C_{sp^2}–O bond in the following phosphorus compounds: triphenyl phosphite[159], pyrocatechol phosphites[153], and 2-aryloxy-1,3,2-dioxaphosphorinanes[30]. In all cases the dipole moment of the C_{sp^2}–O bond (0.3–0.8 D) is directed towards the oxygen atom; this indicates inhibition of $p-\pi$ conjugation. The σ-acceptor transfer of electron density in the direction of the oxygen atom is of comparable magnitude to the π-donor transfer, and predominates in these systems.

The second fragment, that is the P–O bond, can now be considered. In symmetrically substituted trialkyl phosphites, the polarity of this bond is zero[16]. In 2-X-1,3,2-dioxaphosphorinanes, the magnitude and direction of the dipole moment of the bond change with change in the nature of the substituent X (see Table 1),[16,59] and in the aryloxy-derivatives (X = OAr) the ring and exocyclic P–O bonds are non-equivalent and have different polarities[30]: the former have a dipole moment of 0.8 D, directed towards the phosphorus atom, whereas the dipole moment of the second atom is 0.22 D and is directed towards the oxygen atom, that is overall, electron density is transferred from the ring oxygen atoms towards the exocyclic P–O bond, which has clearly defined electron-acceptor properties. The transfer is analogous to that observed in 2-chloro-1,3,2-dioxaphosphorinane, where the P–Cl bond acts as acceptor[16]. σ-Acceptor transfer of electron density towards the oxygen atom also follows from an analysis of the dipole moments of pyrocatechol phosphites[153].

The data obtained from dipole moments on the polarity of the P–O bond in the P–O–Ph fragment exclude the possibility of π-acceptor interaction of the UEP of the oxygen atom with the phosphorus-containing group (p_π–d_π conjugation or hyperconjugation). In all the examples studied, the P–O–Ph fragment behaves as an electron density acceptor.

c) Bond Lengths

The additional bonding produced as a result of the conjugation effect (including p–π and p_π–d_π conjugation) is reflected in changes in the bond lengths. Increase in the length of a bond indicates a decrease in its double bond character and an increase in its antibonding character. For example, the C–O(Ph) bond length increases from 1.361 Å in anisole (XXXV) [160] to 1.38 Å in the sterically strained compound (XXXVI),[161] in which the methoxy groups are displaced from the plane of the benzene ring. In *p*-fluoroanisole, theoretical calculations have established an increase in the length of the C–O(Ph) bond by 0.014 Å on going from the planar to the orthogonal structure[162]. Table 4 gives the results of an X-ray diffraction study of the bond lengths in O-phosphorylated phenols. In all cases, an increase (by 0.03–0.05 Å) is observed in the C–O(Ph) bond length, indicating a decrease in its double-bond character compared with anisole and even with its sterically strained analogues.

The characteristics of phosphorus–ether bonds can also change with change in the type of intramolecular electronic interactions. The data in Table 4 show that in most cases [except compound (XXX)], the bonds next to Ar are longer than the P–O(Alk) bond, indicating that there is no additional bonding in the P–O(Ar) fragment. Thus this fragment has greater acceptor character than the P–O(Alk) group. For all the cyclic compounds given (XXVI)–(XXXII), the endo- and exocyclic P–O bonds are non-equivalent. In 1,3,2-dioxaphosphorinanes with a phenoxy group in the axial position, (XXVI)–(XXIX) and (XXXI), the increase in the antibonding character of the exocyclic bond is greater, and the bond is 0.02–0.03 Å longer than the ring bonds.

This effect is not related to a change in the nature of the substituent (Alk or Ar) on the O atom, since it is also observed in the compounds (XXXI) and (XXXII),[151,152] although in the last case the increase in the antibonding character of the P–O(Ar) bond is greater. This difference is related to the conformational characteristics of the bonds: in 1,3,2-dioxaphosphocine[152] and also in the bicyclic *trans*-isomer of 1,3,2-dioxaphosphorinane (XXX),[166] the exocyclic P–O(Ph) bonds occupy the *e* position, in contrast to all other compounds, where this bond is in the axial position. For the *e* position there is a change in the three-dimensional structure of the entire P–O–Ph fragment; from the "*cis*" conformation characteristic of the *a*-phenoxyl group,[30,136,150,151,163] the phenyl group changes to the T structure relative to the UEP of the P atom[152]; 1,3-synaxial interactions do not prevent the production of the T conformation. Change in the confirmations also leads to a change in the bond lengths: the conformations of the ring and exocyclic P–O bonds in compounds with the OPh group are described by the TTC [or TTG for P(IV)] structure, and with the *e* group by the GG'T structure. In all the examples given in Table 4, an increase in length is observed for the bonds characterised by the T conformation.

d) Photoelectron Spectra

Unfortunately, almost no studies have been carried out for compounds containing the P–O–Ph fragment. The photoelectron spectra of phenyl dichlorophosphate have been published[168]; splitting of the $\pi(b_1)$ and $\pi(a_2)$ orbitals of the benzene ring was not detected, and this may indicate that there is no p–π conjugation.

e) ^{13}C NMR Spectra

The π-electron density distribution in derivatives of phenol and anisole can also be estimated from the chemical shifts in the ^{13}C NMR spectra;[142,169,170] here, the changes in the chemical shifts of the carbon atom in the *para*-position of the benzene ring are due to the effect of conjugation. In alkyl phenyl ethers, with inhibition of p–π conjugation, a decrease in the shielding of C_n compared with anisole was detected[145,158,170]. According to published data, in O-phosphorylated phenols[171,172] and anilines[173] the deshielding of the C_n atom increases and reaches 2.7–6.3 p.p.m. The weak-field displacements of the C_n signal in phosphorus compounds (by analogy with systems in which steric inhibition of the p–π conjugation effect is observed) can be attributed to a decrease in or even the absence of interaction between the p orbitals of the oxygen atom and the π orbitals of the benzene ring.

f) Ultraviolet Spectra

The participation of the π-electron of the benzene ring in conjugation with the UEP of the oxygen atom can be studied from the ultraviolet spectra; it is revealed in a bathochromic shift and an increase in the intensity of the λ_2 and λ_1 absorption bands of benzene (in anisole, 217 nm, ε = 8050; 271 nm, ε = 1500 [140]). In t-butyl phenyl ether and 2,6-dimethylanisole, where conjugation is sterically inhibited, the intensity of the λ_3 band is low (460,[174] 334 [146]).

The ultraviolet spectra of derivatives of 2-phenoxy-1,3,2-dioxaphosphorinanes have been studied[172].

For the 2-oxide and the 2-sulphide, a complete analogy with the spectra of the sterically strained anisoles is observed: the λ_2 band does not undergo the bathochromic shift characteristic of anisole, the fine vibrational structure of the λ_3 band is preserved, and its intensity does not exceed 440. The general form and position of the λ_3 band are also preserved for the compound with P(III), ε_{max} = 520. The analysis of the λ_2 band is made difficult by the presence of

additional absorption in the region of ~200 nm, due to the $n-\sigma^*$ transfer of the UEP of the P(III) atom[172,175]. The preservation of the autonomous organisation of the benzene ring in 2-phenoxy-1,3,2-dioxaphosphorinanes indicates that $p-\pi$ conjugation is inhibited in these compounds. Additional analysis of *p*-bromo- and *p*-alkyl-substituted dioxaphosphorinanes indicates that the O-phosphorylated group has electron-acceptor properties[172].

g) Reactivity

The study of the ionisation constants and reactivity of pyrocatechol phosphites and other cyclic systems containing the P–O–Ph fragment indicates an increase in the acceptor properties of these groups, compared with the analogous systems in which the phenyl group is replaced by an alkyl group[176,177]. A fundamental difference has been detected in the distribution of the products of the nitration of acetyl and phosphorylated derivatives of aniline and phenol; in the organophosphorus compounds, nitration takes place more rapidly in the *m*-position, and not in the *o*- and *p*-positions, as in the derivatives of aniline and phenol[178]. The authors cited[178] consider that this difference cannot be explained on the basis of existing ideas about the effects of substituents. Data on the dual behaviour of the oxygen atom, depending on the nature of the substituents round it, make it possible to attribute the preferential formation of the *m*-products in the nitration of O- and N-phosphorylated phenols and anilines to the acceptor properties of the oxygen atom in these systems.

2. THEORETICAL EXAMINATION

The above experimental data show that fairly extensive material has now accumulated on the three-dimensional and electronic structure of O-phosphorylated phenols and their chemical behaviour, indicating that the phosphorus-containing group has a specific influence on the nature of the interaction between the phenyl group and a neighbouring oxygen atom on the one hand, and the oxygen atom and the phosphorus-containing group on the other. The data obtained, that is the approximately orthogonal orientation of the π-orbitals of the benzene ring and the *p*-orbitals of the UEP of the oxygen atom, the change in the direction of the dipole moment of the C_{sp^2}–O(P) bond compared with anisole, the preservation of the autonomous organisation of the absorption bands of the benzene ring in the ultraviolet spectra, and the increase in the acceptor properties of the P–O–Ph fragment compared with P–O–Alk, show that the predominant properties are not the π-donor properties usually observed for organic oxygen compounds, but σ-acceptor properties. In the O–C_{sp^2}(Ph) fragment, $p-\pi$ conjugation is inhibited, and in the P–O(Ar) group the signs of π-acceptor interaction are poorly defined. The dual behaviour of the O atom is due to the difference in the electronic structure of the substituents on it[179].

A theoretical examination by the non-empirical SCF method has shown that the σ-acceptor power of the oxygen atom is increased if the neighbouring fragment has a low-lying lowest unoccupied molecular orbital LUMO.[179] These properties are characteristic of the bonds formed by the phosphorus atom. According to the photoelectron spectra, their ionisation potentials are lower than the ionisation potentials of ether bonds[15]. This indicates an increase in the energy of the σ-occupied molecular orbitals, and probably a corresponding decrease in the energy of the LUMO.

The difference in the strength of the manifestation of the effect for P(III) and P(IV) compounds is also explained on the basis of these concepts. The bonds in the P(IV) compounds are more stable, as revealed by the fact that the P^{IV}–X bonds are shorter than the P^{III}–X bonds, and is detected thermochemically[5]. As noted above, the additional increase in the antibonding character of the bonds in the P(III) compounds is due to the α-effect. The increase in the antibonding character leads to a decrease in the energy of the σ-orbitals of the bonds and an increase in the strength of the manifestation of the π-acceptor properties of the O atom.

The dependence of the effect on the spatial characteristics was noted above. For P–O bonds, the greatest increase in antibonding character is observed in the T conformation (section II), in which the *p*-orbital of the UEP of the neighbouring oxygen atom is close to the T-position relative to the P–O bond, so that steric conditions are created for $n_O-\sigma^*_{P-O}$ interaction. This approach makes it possible to explain the non-equivalence of the P–O bonds in cyclic aryl phosphites (Table 4). The interaction affects the whole O_2POAr group, and is so effective that it is able to block the $p-\pi$ conjugation between O and Ar.

The additional compensation may be related to $\pi-\sigma^*$ interaction, so characteristic of benzyl halides[180–185], methylallylsilanes[186], and benzylphosphines[92]. A necessary condition for this interaction is the mutually perpendicular arrangement of the plane of the benzene ring and the σ-bond.[184,185] Fig. 3 shows that it is also fulfilled for O-phosphorylated phenols. An analysis of 2-phenoxy-1,3,2-dioxaphosphorinanes[30,172] shows that the picture of the electron density distribution in these compounds is consistent with this interaction: electron density is transferred from the phenyl group towards the oxygen atom.

Thus the introduction of a phosphorus atom next to an aryloxy fragment radically alters the nature of the orbital interactions of the central oxygen atom with neighbouring fragments, one of which contains π-electrons (the benzene ring), while the other is a strong π-acceptor (the phosphorus-containing group). The inhibition of $p-\pi$ and $p_\pi-d_\pi$ conjugation and the change in the nature of the electron density distribution and chemical reactivity of the compounds indicates that the predominant properties in these systems are not the usual π-donor but the σ-acceptor properties of the oxygen atom, due to the proximity to a low-lying unoccupied molecular orbital of the phosphorus-containing group of atoms.

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A systematic combined examination of the spatial and electronic characteristics of P(III) and P(IV) bonds has revealed the exceptional importance of many types of specific orbital interactions with low-lying unoccupied π^* and σ^* orbitals of the phosphorus bonds. It was previously assumed that these interactions did not take place or played an insignificant role in organic compounds. In recent years, the position has changed. Analysis of the conformational behaviour of a number of organic molecules has shown that these interactions play an important role in determining the three-dimensional structure of molecules of this kind[1,2]. Even for butadiene, which has become the classical example of a compound in which $\pi-\pi$ conjugation predominates, recent non-empirical calculations have shown that the energy of conjugation in the planar form is only slightly (~1.5 kcal $mole^{-1}$)

greater than the energy of hyperconjugation in the perpendicular conformation[187]. In phosphorus compounds, the acceptor power of the bonds is much greater, as a consequence of the decrease in the energy of the π^* or σ^* orbitals. Unfortunately, there are no accurate quantitative data.

The CNDO/S method has been used to estimate the energy of the π^* orbitals of the PX_2 fragment in vinylphosphine oxides. It amounts to 0.82 eV for X = F, −0.80 eV for X = Cl, and 2.34 eV for X = OMe; on going to the corresponding methyl derivative, the energy increases sharply to 6.0 eV.[188] Indirect confirmation of the marked decrease in the energy of the unoccupied orbitals of the bonds compared with organic compounds is provided by the decrease in the ionisation potentials of the phosphorus bonds, which indicates an increase in the energy of the occupied MO and apparently a corresponding decrease in the energy of the LUMO. The increase in the acceptor power of the P bonds compared with N is not an exception, and is characteristic of all elements of period III. It is a maximum in P(III) compounds as a consequence of the destabilising effect of the repulsion of the UEP of adjacent heteroatoms. The reasons for the decrease in the acceptor properties of P(IV) bonds compared with P(III) were noted above.

All the above material reveals the close relationship between the effects of the mutual influence of atoms and the three-dimensional structure of organophosphorus compounds. The nature of orbital effects is closely related to the conformational characteristics of the interacting orbitals: the effect of $n-\sigma^*$ hyperconjugation predominates for the *trans*-orientation of the orbital of the UEP and the σ-polar bond, whose acceptor properties are a maximum with the destabilising $n-n$ repulsion of the UEP of the adjacent heteroatoms forming this bond (the α-effect); $\pi-\sigma^*$ interaction in $ArPX_2$ becomes decisive with the parallel orientation of the π-orbitals of the benzene ring and $\pi^*_{PX_2}$, leading to the production of the bisector form. The same structural restrictions are revealed in P–O–Ar systems. From the last example it can be seen that the introduction of a phosphorus atom into organic compounds leads to changes in the nature of the electronic interactions not only in the groups directly adjoining this atom, but also in neighbouring fragments.

Comparison of the physical properties of compounds with their three-dimensional structure makes it possible to take a fresh look at the nature of the orbital interactions. Traditional theoretical ideas often not only cannot predict but even cannot explain the observed changes in various properties of the bonds in OPC. The present review presents clear proof that so-called "non-specific" electronic interactions often predominate. In the opinion of the present author, they can be called non-specific only in relation to organic compounds; as far as OPC are concerned, they are typical. For example, the above model of the destabilisation of the σ-bond in the T-position to the p orbital of the UEP of a heteroatom ($n-\sigma^*$ interaction) is being used increasingly to explain the reactivity of organic[189] and organophosphorus[18,190–192] compounds.

The present review gives the available experimental data for phosphorus compounds. Many of the above characteristic features, however, are also observed for the compounds of other elements of periods III and IV.[52–56] Thus for aryloxy-derivatives of S and Si, as for O-phosphorylated phenols, stabilisation of the structure with the orthogonal orientation of the p and π orbitals has been detected[155–157], and it has been reported[193] that there is no $p_\pi-d_\pi$ conjugation between the Si and O atoms in these systems. The combined study of the compounds by different physical methods, together with an analysis of the spatial characteristics, will make it possible to find a final theoretical basis for the observed phenomena.

An attempt has been made above to classify the observed effects from the viewpoint of perturbation theory. The problem examined requires a penetrating theoretical description at a higher level. There are grounds for hoping that the use of non-empirical methods of calculation will make an important contribution to the elucidation of the characteristic features of intramolecular electronic interactions in OPC. Moreover, there have as yet been few rigorous experimental studies to establish the nature, mechanism, and spatial-directed character of the effects of the mutual influence of atoms in phosphorus compounds (this applies particularly to photoelectron and X-ray spectroscopic studies).

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Butlerov Chemical Scientific Research Institute

Ul'yanov-Lenin Kazan' State University

Translated from *Uspekhi Khimii*, 53, 625-650 (1984) U.D.C. 547.1'181.54

Tertiary Phosphines with Functional-group Substituents

O.A.Erastov and G.N.Nikonov

The methods of synthesis of substituted tertiary phosphines and the characteristic features of the mutual influence of the phosphino-group and the substituent, manifested in physicochemical properties (equilibrium between the conformers or stereoisomers, geometrical parameters of the molecules) and in the reactivity (pathways leading to the decomposition of phosphonium compounds, reactions of functional groups with electrophiles, nucleophilic substitution, tautomerism, rearrangements), are examined.
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I. INTRODUCTION

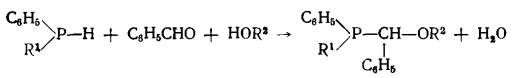
Tertiary phosphines containing electron-accepting substituents possess a high and varied reactivity. Firstly, they enter into reactions typical for tertiary phosphines and the functional groups present. The mutual influence of the active centres is manifested in the reaction rates and in the stability of the products formed. Secondly, features determined by the presence of closely linked functional groups are characteristic of such compounds. They react with electrophiles to form phosphonium compounds which are unstable and are stabilised as a result of proton transfer to the negative centre of the electrophile with formation of new tertiary phosphines or ylides. These reactions exhibit an analogy in reactivity between tertiary phosphines with functional-group substituents and primary or secondary phosphines and also esters of tervalent phosphorus acids. The presence of an electron-accepting substituent facilitates nucleophilic substitution at the carbon atom attached to the phosphorus atom and both the phosphino-group and the functional group can be eliminated. The closeness in space of the phosphino-group and the substituent creates favourable conditions for rearrangements. The accumulation of electron-accepting substituents at the carbon atom attached to the phosphorus atom leads to prototropic diad phosphorus–carbon tautomerism.

The synthesis of tertiary phosphines with functional-group substituents is based on the available starting material such as phosphine, tervalent phosphorus acid chlorides, and white phosphorus. It is therefore not surprising that during the last decade there has been a rapid development of the chemistry of compounds of this class and many investigations, which need to be surveyed, have been published. This review deals with the methods of synthesis and properties of tertiary phosphines with functional-group substituents. These problems have been partly discussed in other communications[1-5].

II. METHODS OF SYNTHESIS

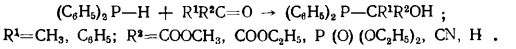
Tertiary phosphines with functional-group substituents can be obtained from phosphines, silylphosphines, phosphides, tervalent phosphorus acid chlorides, and derivatives such as phosphonium salts, phosphine oxides, and phosphine sulphides.

The most general method of synthesis involves the addition of phosphines via the P–H bond to unsaturated compounds. Phosphine[1] and primary and secondary phosphines[6-10] react with aldehydes in a neutral medium to form α-hydroxyalkylphosphines. Halogen-containing aldehydes also enter into the reaction; thus crystalline tris(α-hydroxy-β,β,β-trichloroethyl)phosphine has been obtained from PH_3 and chloral[11]. α-Alkoxyalkylphosphines are formed in the presence of alcohols[12]:



R^1=CH_3, C_6H_5; R^2=CH_3, C_2H_5, iso-C_3H_7, C_4H_9 .

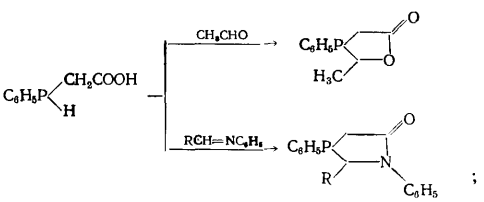
Ketones react similarly to aldehydes. Substituents do not influence the mode of reaction. α-Alkoxycarbonyl-α-hydroxyethylphosphines have been obtained by reaction with pyrubic acid esters[13,14]:



R^1=CH_3, C_6H_5; R^2=$COOCH_3$, $COOC_2H_5$, P (O) $(OC_2H_5)_2$, CN, H .

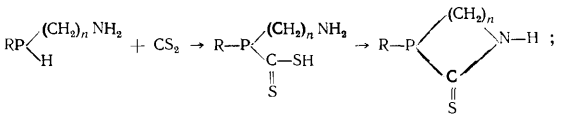
The addition of phosphines to thiobenzophenone[15], azomethines[16], isocyanates, and carbodi-imides[17,18] has been described. The interaction of phenylphosphine with azomethines and benzaldehyde leads to the formation of *N*-substituted 2,4,5,6-tetraphenyl-1,3,5-oxazaphosphorinanes[19].

The addition of primary and secondary phosphines to ethylenesulphonyl fluoride[20], vinyl sulphones[21], vinylsilanes[22,23], vinylphosphines[24], allylamines[25], and unsaturated acid esters[26] has led to the corresponding β- and γ-substituted tertiary phosphines. The reactions of primary phosphines take place stepwise and can be arrested in the first stage, which makes it possible to substitute the hydrogen atoms in succession by various functional groups. 1,3-Azaphospholan-5-ones and 1,3-oxaphospholan-5-ones[27,28], 1,3-oxaphospholans[29], 1,3-oxaphosphorinanes[30], and 1,3-azaphosphepanes[31] have been obtained in this way, for example:



$R=CH_3$, C_2H_5, C_6H_5 .

The introduction of carbon disulphide into the reaction with aminoalkylphosphines made it possible to obtain 1,3-azaphospholanes and 1,3-azaphosphorinanes with thiocarbonyl groups in the ring[32]:



n=2, 3; R=C_4H_9, C_6H_5, cyclo-C_6H_{11} .

Acylphosphines[33] and γ-hydroxypropylphosphines[34] have been obtained by the addition of phosphines to ketens and oxetan respectively.

Tertiary phosphines with functional-group substituents can be obtained from phosphines also with the aid of the substitution reaction. Aminomethylation of phosphines by alkoxymethylamines and diaminomethanes yielded aminomethylphosphines[35-37]:

$$R^1R^2PH + R_2^3NCH_2OCH_3 \rightarrow R_2^3NCH_2PR^1R^2 ;$$

R^1= iso-C_3H_7, t-C_4H_9; R^2= iso-C_3H_7, $CH_2C_6H_5$;

R_2^3=O $(CH_2CH_2)_2$;

$$[(CH_3)_2N]_2CH_2 + R_2PH \rightarrow (CH_3)_2NCH_2PR_2 ;$$

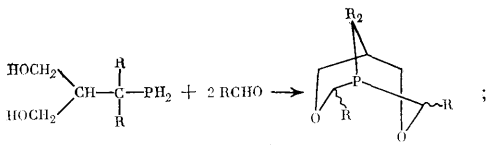
R= iso-C_3H_7 .

Secondary phosphines react with orthoformates in the presence of BF_3 at 20 °C to form phosphinoformals[38]:

$$R_2P{-}H + HC(OR)_3 \rightarrow R_2PCH(OR)_2 + ROH$$

R=C_2H_5, C_4H_9

3,7-Dioxa-1-phosphabicyclo[3.3.1]nonanes have been synthesised by the reaction of aldehydes with a primary phosphine containing two β-hydroxy-groups[39]:



R = H, CH_3, iso-C_3H_7 .

Silylphosphines are used widely to obtain tertiary phosphines with functional-group substituents. Like phosphines, which contain the P—H bond, silylphosphines react with carbonyl compounds to form siloxyalkylphosphines[40-42]:

$$R_n^1P(SiR_3^2)_{3-n} + (3-n)R^3CHO \rightarrow R_n^1P\left(CHOSiR_3^2\right)_{3-n} ;$$

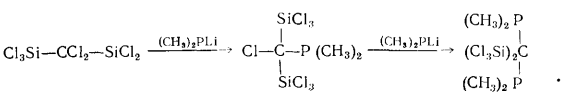
n=1, 2; R^1=C_6H_5; R^2=CH_3; R^3=H, C_6H_5, C $(CH_3)_3$, CN .

Reactions of diorganylsilylphosphines with carboxylic acid chlorides yield acylphosphines[40,43-45]. The trimethylsilylphenyl group adds to carbodi-imides[18] and substitues the chlorine atom in dichloromaleic ester[46].

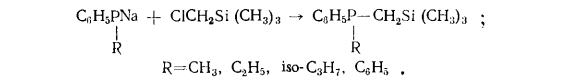
In the reactions with halogen-containing compounds, it is possible to employ metal phosphides instead of silylphosphines. Trialkoxycarbonylphosphines have been obtained from sodium phosphide and chlorocarbonic acid esters[47], while trifluorovinylphosphines are formed in small amounts from lithium phenylphosphides and trifluorovinyl halides[48]. Lithium or sodium phenyl- and methyl-phosphides react with 3-chloropropyldiphenylphosphine to form γ-diphosphines[49]. The reaction of sodium diphenylphosphide with methylene chloride results in the formation of tetraphenylmethylenediphosphine[50]:

$$2(C_6H_5)_2PNa + CH_2Cl_2 \rightarrow (C_6H_5)_2PCH_2P(C_6H_5)_2 .$$

α-Chloromethyldimethylbis(α-trichlorosilyl)phosphine, which is capable of undergoing many further transformations, has been obtained from lithium dimethylphosphide. The substitution of the mobile chlorine atom in this compound leads to new derivatives of tertiary phosphines[51]:

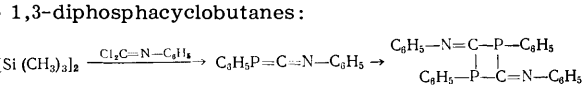


Together with the electron-accepting substituents enumerated above, the use of metal phosphides has made it possible to introduce the electron-donating trimethylsilylmethyl group in the α-position with respect to the phosphorus atom[52]:

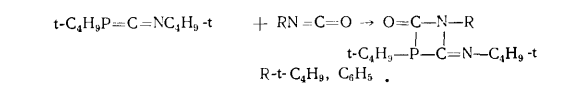


R=CH_3, C_2H_5, iso-C_3H_7, C_6H_5 .

One of the methods of synthesis of heterocyclic phosphines with functional-group substituents is the dimerisation of compounds of dicoordinate phosphorus. The interactions of disilylphosphines with carbon disulphide[53] or phenyl isocyanide dichloride[54], of lithium silylphosphide with carbonyl compounds[55], and of disilylphosphines and primary phosphines with ketones and dimethylformamide[56] lead to the formation of compounds with a dicoordinate phosphorus atom, which dimerise to 1,3-diphosphacyclobutanes:



The cycloaddition of isocyanates to "carboimidophosphene" yields 1,3-azaphosphetidines with imino- and carbonyl groups[57]:



R-t-C_4H_9, C_6H_5 .

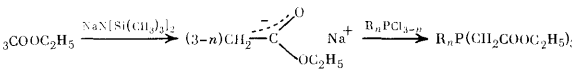
Tervalent phosphorus acid chlorides readily react with compounds having a mobile hydrogen atom or with organometallic compounds. The abstraction of hydrogen chloride by triethylamine has been observed in the phosphorylation of methyl trifluoromethyl sulphone and malonic acid esters by chlorodialkylphosphines[58,59]:

$$CH_3SO_2CF_3 + (C_2H_5)_2PCl \rightarrow (C_2H_5)_2PCH_2SO_2CF_3 + HCl ;$$
$$CH_2(COOR)_2 + (C_2H_5)_2PCl \rightarrow (C_2H_5)_2PCH(COOR)_2 + HCl ;$$

R=CH_3, C_2H_5 .

This yielded tertiary phosphines with trifluoromethanesulphonyl and alkoxycarbonyl groups. The latter are also formed in the phosphorylation of triethylstannylacetic acid esters[60] and sodio-derivatives of carboxylic acid esters having the enolate structure[61]:

$$2(C_2H_5)_3SnCH_2COOC_2H_5 + RPCl_2 \rightarrow RP(CH_2COOC_2H_5)_2 ;$$
R=CH_3, C_6H_5 ;



R= iso-C_3H_7, C_6H_5; n = 0, 1, 2 .

The interaction of tetrachloromethylenediphosphine with organomagnesium compounds leads to diphosphinomethanes[62]:

$$Cl_2PCH_2PCl_2 \xrightarrow{4RMgCl} R_2PCH_2PR_2 ;$$
R=CH_3, C_2H_5, iso-C_3H_7, s-C_4H_9, C_6H_5 .

The phosphorylation of the lithio-derivatives of these compounds makes it possible to introduce yet another phosphino-group[63,64]:

$$LiHC[P(CH_3)_2]_2 + (C_6H_5)_2PCl \rightarrow (CH_3)_2P{-}CH(P(C_6H_5)_2){-}P(CH_3)_2 .$$

Di- and tri-(*o*-hydroxyphenyl)phosphines[65] phosphorus-containing alkenes[66], and 2-vinylphosphiran[67] have also been obtained from organometallic compounds and phosphorus chlorides:

$$o\text{-}LiOC_6H_4Li + PCl_3 \rightarrow (o\text{-}HOC_6H_4)_3P;$$

$$(C_6H_5)_2PCl + BrMgCH{=}CHR \rightarrow (C_6H_5)_2PCH{=}CHR;$$

$R = CH_3,\ C_6H_5;$

$$RPCl_2 + \overbrace{MgCH_2CH{=}CHCH_2} \rightarrow \overbrace{RP(-CH_2CHCH{=}CH_2)}$$

$R = CH_3,\ C_6H_5,\quad t\text{-}C_4H_9.$

The methods of synthesis of tertiary phosphines with functional-group substituents and the corresponding derivatives of quinquevalent phosphorus, namely phosphonium salts, phosphine oxides, and phosphine sulphides, are also important. The cleavage of tetra(hydroxymethyl)phosphonium salts by bases yields tri(hydroxymethyl)phosphine[1,68]. Tertiary phosphines can be used as the bases[69]:

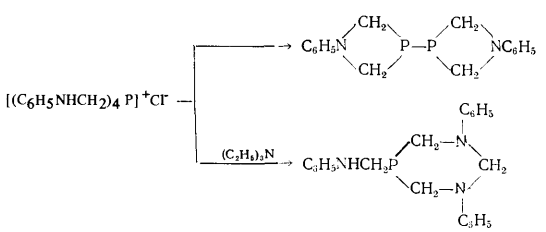
$$[(HOCH_2)_4P]^+Cl^- + (C_4H_9)_3N \rightarrow (HOCH_2)_3P + [(C_4H_9)_3PCH_2OH]^+Cl^-$$

When tetra(chloromethyl)phosphonium chloride is treated with alkali, tri(chloromethyl)phosphine is formed[70]:

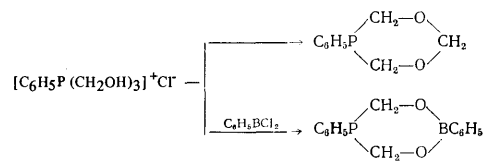
$$[(ClCH_2)_4P]^+Cl^- \xrightarrow{NaOH} (ClCH_2)_3P.$$

Methylcarbamate derivatives of tri(hydroxymethyl)phosphine have been obtained from methylcarbamate derivatives of phosphonium salts[71].

The disproportionation of phosphonium salts involves the formation of various products including tertiary phosphines with functional group substituents. Refluxing of tetra-anilinomethyl)phosphonium chloride in ethanol leads to the formation of 1,1'-diphenyl-1,1'-diaza-3,3'-diphosphetidine[72], while its treatment with triethylamine gives rise to 5-anilino-methyl-1,3-diphenyl-1,3,5-diazaphosphorinane[73]:



2,5-Diphenyl-1,3,2,5-dioxaboraphosphorinane has been obtained by heating tri(hydroxymethyl)phenylphosphonium chloride with dichlorophenylborane[74]. 5-Phenyl-1,3,5-dioxaphosphorinane is formed in the absence of dichlorophenylborane[75]:



There exist examples of the reduction of phosphine oxides containing fucntional groups. Many aromatic tertiary phosphines containing hydroxy-, cyano-, alkoxycarbonyl, and formyl groups as well as other substituents in the *ortho*-, *meta*-, and *para*-, positions in the aromatic ring have been obtained in this way[76,77]. Trichlorosilane has been used as the reducing agent. The oxides can be converted into sulphides in a preliminary step with subsequent removal of sulphur by treatment with triphenyl phosphite[78]:

$$(ClCH_2)_2\overset{O}{\overset{\|}{P}}Cl \xrightarrow{P_2S_5} (ClCH_2)_2P(S)Cl \xrightarrow{(C_6H_5O)_3P} (ClCH_2)_2PCl \xrightarrow{RMgBr} (ClCH_2)_2PR;$$

$R = CH_3,\ C_2H_5.$

The products of the addition of hypophosphorous acid to unsaturated compounds[79,80] as well as tertiary phosphine oxides with nitro-[81], amino-[82,83], phenoxy-[84], and alkoxycarbonyl groups[5], particularly those obtained from white phosphorus[85], are of interest as compounds to be reduced.

In addition to the above discussion, attention should be drawn to the possibility of obtaining tertiary phosphines with functional-group substituents by adding aluminophosphines[86] and germylphosphines[87] to unsaturated compounds:

$$R_2AlP(C_6H_5)_2 \xrightarrow{R^1C\equiv N} R_2AlN{=}CR^1P(C_6H_5)_2;$$

$R = C_6H_5,\ n\text{-}CH_3C_6H_4,\ изо\text{-}C_4H_9;\ R^1 = C_6H_5,\ CH_3;$

$$(CH_3)_3GeP(CH_3)_2 \xrightarrow{(CH_3)_3SiC(O)C_6H_5} (CH_3)_3GeC(C_6H_5)P(CH_3)_2.$$

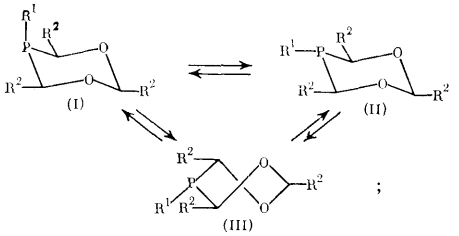
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OSi(CH_3)_3$$

The last reaction proceeds with a rearrangement.

III. PHYSICOCHEMICAL PROPERTIES

Tertiary phosphines with functional-group substituents contain two or more groups capable of interacting with one another. Such interaction should lead to the appearance of unusual features in the structure and reactivity of the compounds. The position of equilibrium between the conformers or stereoisomers and the geometrical characteristics of the molecules are the most sensitive to the mutual influence of atoms.

The equilibrium between the conformers of unsubstituted 1,3,5-dioxaphosphorinanes or between the stereoisomers of their substituted derivatives has been investigated[88–97]:

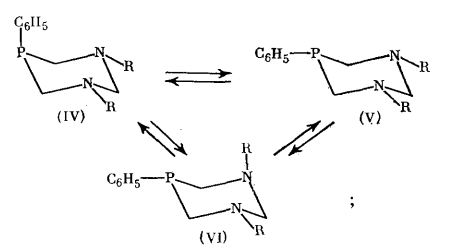


(I) ⇌ (II); (I) ⇌ (III); (II) ⇌ (III);

$R^1 = H,\ CH_3,\ C_6H_5,\ Cl;\ R^2 = H,\ CH_3,\ iso\text{-}C_3H_7,\ C_6H_5.$

The contents of form (I) in the equilibrium (I) ⇌ (II) with $R^1 = C_6H_5$ are 72 and 86% for $R^2 = H$ and CH_3 respectively. In the case of 1-phenylphosphorinane[98], 4-t-butyl-1-phenylphosphorinane[99], and 1-phenylphosphorinan-4-ones[100–102], its content is 30–40%. Comparison shows that the replacement of the CH_2 group by the oxygen atom shifts the equilibrium towards form (I). This effect indicates the interaction between the heteroatoms and is anlogous to that observed in heterocycles with the N–C–O fragment[103–105].

The equilibrium between the conformers of *N*,*N*-disubstituted 5-phenyl-1,3,5-diazaphosphorinanes has been studied[106,107]:

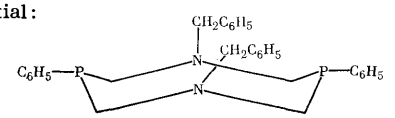


(IV) ⇌ (V); (IV) ⇌ (VI); (V) ⇌ (VI);

$R = C_6H_5,\ C_6H_4CH_3\text{-}p,\ C_6H_4Br\text{-}p,\ CH_2C_6H_5.$

In the case of aryl substituents at the N atoms, conformer (VI) is absent from the equilibrium. The contents of form (IV) in the equilibrium (IV) ⇌ (V) are 24,34, and 0% for R = C_6H_5, $C_6H_4CH_3$-*p*, and C_6H_4Br-*p* respectively. 1,3-Dibenzyl-5-phenyl-1,3,5-diazaphosphorinane is a mixture of conformers (V) and (VI) (64:36). This has been confirmed by X-ray diffraction[107]; it was found that in the crystalline state the compound has the chair conformation with axial orientation of the benzyl group at one of the N atoms. In terms of the position of the conformer equilibrium, 1,3-dibenzyl-5-phenyl-1,3,5-diazaphosphorinane differs little from 1,3-dimethyl-1,3-diazane (40% of the form with the axial orientation of the methyl group[104]). Hence it follows that in 1,3,5-diazaphosphorinanes there is an interaction between the N atoms in which the P atom is not involved.

In the case of 1,5-diaza-3,7-diphosphacyclo-octanes, there are no competing interactions, which makes it possible to solve the problem of the mutual influence of the atoms in the P–C–N system. According to X-ray diffraction data[108], 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclo-octane exists in the crown conformation. The P and N atoms are involved in a trigonal-pyramidal coordination (the sums of the valence angles are 297° and 343° respectively). The positions of the phenyl groups at the P atoms are pseudo-equatorial while those of the benzyl groups of the N atoms are pseudoaxial:



The pseudoaxial orientation of the substituents at the N atoms can be regarded as a consequence of the interaction between the heteroatoms in the P–C–N system; it is analogous to that observed in the N–C–N system[103–105].

According to one concept[109], the interaction between the heteroatoms in the N–C–O and N–C–N systems, stabilising the axial orientation of the substituent at the N atom, involves the transfer of electron density from the orbital of the unshared electron pair of the nitrogen atom to the unoccupied orbital of the C–O or C–N bond. From this standpoint, the electron shifts in the P–C–O and P–C–N systems should be of different types, since they stabilise the axial orientation of the substituent at the P atom in the former case and of the substituent at the nitrogen atom in the latter case.

The influence of the interaction of the groups in tertiary phosphines with functional-group substituents can be manifested not only by the position of the conformational equilibrium or the equilibrium between the stereoisomers but also by other characteristics of the molecule: bond lengths, bond angles, dipole moments, NMR parameters, etc. 2,6,7-Trioxa-4-phosphabicyclo[2.2.2]-octanes are of interest in this connection. There exist X-ray diffraction data for the bicylcic phosphorothioate $S{=}P(OCH_2)_3P$ and its derivatives[110] as well as the complex $P(OCH_2)_3P.Fe(CO)_5.P(OCH_2)_3P$.[111] The P–C bond lengths and valence angles at the phosphorus atoms in these compounds are close to the normal values. The experimental dipole moments of $P(CH_2O)_3P$ (3.10 D) and $P(CH_2O)_3As$ (1.58 D) agree well with the calculated values (2.94 and 1.49 D respectively)[112]. The ^1H NMR spectra of the compound $P(CH_2O)_3P$ and certain analogous bicyclic compounds and their derivatives have been examined[113–116]. The spin–spin coupling constants $^2J_{PH}$ for all phosphorus(III) compounds are close to the expected values; it was not possible to observe deviations in the case of 2,6,7-trioxa-4-phosphabicyclo[2.2.2]octanes.

X-Ray diffraction data for 1,3,5-triaza-7-phospha-adamantane and its derivatives have been published[117,118]. The C–N bond length and the angles at the N atoms are close to the normal values. There are appreciable differences between the P–C bond lengths and the latter deviate from the usual value (1.841 Å). However, it is not possible to find a correlation between the observed changes and the interaction of the heteroatoms.

Such correlation has been postulated for 1,5-dibenzyl-3,7-diphosphacyclo-octane[108] and 1,3-dibenzyl-5-phenyl-1,3,5-diazaphosphorine[107]. The decrease of the C–N bond lengths (on average 1.452 Å) and the increase of the P–C bond lengths (on average 1.888 Å) in the former compound and also the decrease of the C–N bond length to 1.424 Å in the latter compound can be explained by the transfer of electron density from the unshared electron pair orbital of the N atom to the unoccupied orbitals of the P–C and C–N bonds respectively. In tetraphenyl-1,5-diaza-3,7-diphosphacyclo-octane[119] the endocyclic bond lengths agree with those found for 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclo-octane[108].

Apart from the results examined above, there exists also data obtained by X-ray diffraction for 2,4-di-t-butyl-2,4-bis(trimethylsiloxy)-1,3-diphosphetan[120], 4-phosphorinanones[121,122], and complexes of tri(β-cyanoethyl)phosphine[123]. The vibrational spectra of acylphosphines have been investigated[124]. In the liquid phase these compounds exist in the form of a single conformer having a plane of symmetry. The considerable decrease of the barriers to pyramidal inversion of the phosphorus atom in acylphosphines compared with tertiary phosphines have been explained by the conjugation of the unshared electron pair of the P atom with the C=O group in the planar transition state[125].

IV. CHEMICAL PROPERTIES

Tertiary phosphines with functional-group substituents undergo oxidation reactions and addition reactions involving the C atom, which are typical for tertiary phosphines. They give rise to phosphine oxides, sulphides, and selenides, phosphonium salts, and other tertiary phosphine derivatives. The influence of the functional groups is manifested by changes in the rates of reaction and in the stability of the products formed[1]. In addition there are many reactions characteristic of these compounds which are due to the presence of functional groups; these are the substitution reactions on treatment with electrophiles or nucleophiles, prototropic phosphorus–carbon diad tautomerism, and rearrangements.

1. Reactions with Electrophiles

The introduction of electron-accepting substituents leads to the appearance of new pathways to the decomposition of the phosphonium compound formed initially; they are associated with the position of the mobile hydrogen atom in the molecule. If the mobile hydrogen atom is in the α-position relative to the phosphorus atom, the phosphonium compound can be stabilised by its elimination in the form of a proton and an anion, the compound itself being converted into an ylide. When the mobile hydrogen atom is in the β-position with respect to the phosphorus atom, there is a possibility of proton transfer from this position to the anionic centre of the molecule with the dissociation of the P–C bond. As a result, the phosphonium compound can decompose into an unsaturated compound and a new tertiary phosphine. In both cases there is a possibility of a competing reaction involving the nucleophilic centre of the functional group. The anions of tertiary phosphines with functional-group substituents undergo competing reactions.

(a) Phosphines with a Mobile α-Hydrogen Atom

The stabilisation of a phosphonium compound by the elimination of a proton from the α-carbon atom with formation of phosphorus ylides has been observed in the reaction of (diethoxycarbonylmethyl)diethylphosphine with ethyl iodide in the presence of triethylamine[126]:

$$R_2PCH(COOR)_2 \xrightarrow{RI} [R_3PCH(COOR)_2]^+I^- \xrightarrow[-HI]{} R_3P{=}C(COOR)_2 ;$$

$$R = C_2H_5 .$$

Ylides are obtained on disproportionation of (dialkoxycarbonylmethyl)diethylphosphines and diethyl(trifluoromethanesulphonylmethyl)phosphine[127,128] and also on their interaction with chlorodiethylphosphine in the presence of triethylamine[129]:

$$2R_2^1P{-}CHR_2^2 \longrightarrow R_2^1\overset{+}{P}(R_2^1P)\text{–}CR_2^2(H)\text{–}CHR_2^2 \longrightarrow R_2^1P{=}CR_2^2 + CH_2R_2^2 ;$$

$$R_2^1P{-}CHR_2^2 + R_2^1PCl \xrightarrow[-HCl]{} R_2^1P{-}CR_2^2(R_2^1P){-}Cl ;$$

$$R^1 = C_2H_5;\ R^2 = COOCH_3,\ COOC_2H_5 \text{ or } CR_2^2 = CHSO_2CF_3 .$$

The reactions of these compounds with carbon tetrahalides proceeds analogously[130,131]:

$$R_2^1P{-}CHR_2^2 \xrightarrow{CX_4} R_2^1\overset{+}{P}(X)\text{–}CR_2^2(H)\text{–}CX_3 \xrightarrow[-CHX_3]{} R_2^1P(X){=}CR_2^2 ;$$

$$R^1 = \text{alkyl},\ C_6H_5;\ CR_2^2 = CH_2,\ CHSO_2CF_3,\ C(SO_2C_6H_5)_2,\ C(CO_2CH_3)_2;\ X = Cl, Br .$$

The activation of the molecule as a result of the formation of hydrogen bonds involving the functional group can lead to the elimination of the phosphino-group on nucleophilic attack. Similar behaviour has been observed in the interaction of the esters of diphosphinoacetic acids with compounds having a mobile hydrogen atom[132]:

$$R_2^1P{-}CH(COOR){-}PR_2^1 + HX \rightarrow R_2^1PCH_2COOR^2 + R_2^1PX ;$$

$$R^1 = \text{iso-}C_3H_7;\ R^2 = C_2H_5;\ X = OH,\ OC_2H_5,\ NR_2,\ OCOCH_3 .$$

Thus electrophilic substitution reactions leading to an increase of the coordination number of the phosphorus atom are characteristic of phosphines having a mobile α-hydrogen atom.

(b) Phosphines with a Mobile β-Hydrogen Atom

There exist numerous instances of the decomposition of phosphonium derivatives with elimination of a proton from the β-position and the liberation of an unsaturated compound, which results in the formation of a tertiary phosphine. Thus, when tri(hydroxymethyl)-phosphine was treated with alkyl halides, the hydroxymethyl groups were substituted by the alkyl groups[133]. Tri(acetoxymethyl)phosphine reacts analogously in the presence of alkali[134]:

$$P(CH_2OCOCH_3)_3 \xrightarrow{NaOH+RX} [RP(CH_2OCOCH_3)_2(CH_2OH)]^+X^- \xrightarrow[-CH_3O,-HX]{} RP(CH_2OCOCH_3)_2 ;$$

$$R = C_2H_5,\ C_3H_7,\ C_4H_9,\ C_5H_{11},\ C_6H_{13};\ X = Br, I .$$

Dimethyl sulphate has been used together with alkyl halides[135]. In the latter case the interaction of the phosphonium salts with hydrochloric acid leads to the formation of chloromethylphosphine oxides[136].

Tri(hydroxymethyl)phosphine[137] as well as di(hydroxymethyl)phosphines[138] react with acrylonitrile in a neutral medium to form the corresponding β-cyanoethylphosphines. The reaction of tri(hydroxymethyl)phosphine with acrylic acid esters proceeds analogously[139]. In an aqueous alcoholic medium β-cyanoethylphosphines are converted into β-alkoxycarbonylethylphosphines[140].

Substitution products have been obtained in the reaction of alkyldi(hydroxymethyl)phosphines with epoxides[141,142]:

$$R^1P(CH_2OH)_2 + 2H_2C\text{—}CHR^2(O) \rightarrow R^1P(CH_2CHOH)_2 ;$$

$$R^1 = CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9,\ \text{iso-}C_6H_{11};\ R^2 = H,\ CH_3 .$$

The conclusion that intermolecular exchange of hydroxymethyl groups takes place in the case of tri(hydroxymethyl)-phosphine was reached on the basis of the study of the temperature-induced changes in the NMR spectra[143–145]. The possibility of such a reaction has been confirmed by the isolation of tri(α-hydroxyalkyl)phosphines on interaction of tri(hydroxymethyl)phosphines with aliphatic aldehydes[146]:

$$P(CH_2OH)_3 \xrightarrow[-3CH_2O]{3R^1CHO} P(CHOH)_3 \xrightarrow[-HI,-R^1CHO]{R^2I} R^2P(CHOH)_2 ;$$

$$R^1 = CH_3,\ C_3H_7,\ \text{iso-}C_3H_7,\ C_6H_{13};\ R^2 = CH_3,\ C_2H_5,\ C_3H_7 .$$

The hydroxyalkyl derivatives of the phosphines obtained in this way react with alkyl halides. After treatment of the products with triethylamine, the corresponding alkyldi-(α-hydroxyalkyl)phosphines were isolated. They were also obtained from alkyldi(hydroxymethyl)phosphines and aldehydes[146].

The hydroxymethyl groups are also displaced on interaction with unsaturated ketones[147,148]. Imidoylphosphines have been obtained by the reaction of di(hydroxymethyl)-phenylphosphine with isobutyl diphenylborinate in the presence of nitriles[149]:

$$C_6H_5P(CH_2OH)_2 \xrightarrow{\text{iso-}C_4H_9OB(C_6H_5)_2+RCN} C_6H_5P(CH_2\text{—}O)(C=N(H)R)B(C_6H_5)_2 ;$$

$$R = CH_3,\ C_6H_5 .$$

In the absence of nitriles the product is 5-hydroxymethyl-2,2,5-triphenyl-2-borata-5-phosphonia-1,3-dioxan[150].

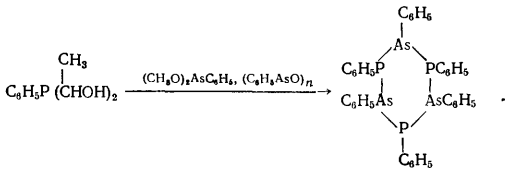
Tri(hydroxymethyl)phosphine reacts with aryl bromomethyl ketones to form aroylmethyltri(hydroxymethyl)phosphonium bromides. Their decomposition by tri(hydroxymethyl)-phosphine results in cyclisation to 4-aryl-1-phospha-3,5-dioxabicyclo[2.2.1]heptanes[151]. The reaction of tris(trimethylsiloxymethyl)phosphine with aryl bromomethyl ketones proceeds differently; when triethylamine is added, hydrogen bromide is split off with formation of ylides[152]:

$$P(CH_2OR^1)_3 \xrightarrow{R^2C_6H_4COCH_2Br} [R^2C_6H_4COCH_2P(CH_2OR^1)_3]^+Br^- \xrightarrow[-HBr]{} R^2C_6H_4COCH{=}P(CH_2OR^1)_3 ;$$

$$R^1 = Si(CH_3)_3;\ R^2 = H,\ CH_3,\ OCH_3,\ Br,\ NO_2 .$$

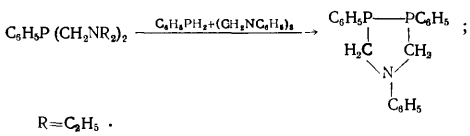
In the former case the reaction proceeds with participation of the β-hydrogen atom and in the latter case with that of the α-hydrogen atom.

There exist examples of the substitution of hydroxyalkyl groups by organoelemental groups. When di(α-hydroxyethyl)phenylphosphine was allowed to react with phenylarsine oxide or dimethyl phenylarsonite, hexaphenyl-1,3,5-triphospha-2,4,6-triarsacyclohexane was obtained[153]:



Aminomethyl groups are also capable of being substituted by organic and organoelemental groups. The reaction of 5-*p*-toluidinomethyl-1,3-di-*p*-tolyl-1,3,5-diazaphosphorinane with methyl iodide led to the isolation, instead of the addition products, of one of the symmetrisation products—5,5-dimethyl-1,3-di-*p*-tolyl-1,3,5-diazaphosphonarinane iodide having two methyl groups at the phosphorus atom[154]. A product with two aminomethyl groups at the phosphorus atom has been obtained by treating di-isopropylmorpholinomethylphosphine with methyl iodide[155]. The overall result of these two reactions is the formation of both symmetrisation products.

When bis(diethylaminomethyl)phenylphosphine is heated with phenylphosphine, diethylmethylamine and diethylamine are produced together with the formation of $(C_6H_5P)_5$ and $(C_6H_5P)_4CH_2$.[156] In the presence of 1,3,5-triphenyl-1,3,5-triazane, the product is 1,3,4-triphenyl-1,3,4-azadiphospholan[157]:



R=C_2H_5 .

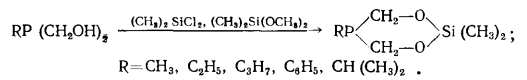
Tri(β-cyanoethyl)phosphine also reacts with methyl iodide to form substitution products[158].

An interesting instance of electrophilic substitution is provided by the reactions of tri(hydroxymethyl)phosphine leading to compounds with a dicoordinate phosphorus atom. Phosphacyanines[159] and 2,4,6-triphenylphosphabenzene[160] have been obtained in this way.

Tris(trimethylsiloxymethyl)phosphine without mobile hydrogen atoms give rise to dihalogenotris(trimethylsiloxymethyl)phosphorane on interaction with PCl_5 and HCl.[161]

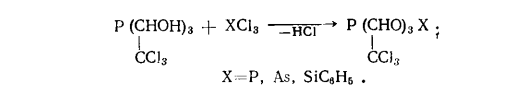
Reactions involving the functional group are extremely characteristic of phosphines having a mobile β-hydrogen atom. The interaction of alkyldi(hydroxymethyl)phosphines with phenyl and *m*-chlorophenyl isocyanates, leading to alkyldi(arylaminocarbonyloxymethyl)phosphines, takes place readily[162]. Alkyldi(hydroxymethyl)phosphines react vigorously with di-isocyanates to form polyurets[163]. Apart from isocyanates, carbonyl compounds have been used as the organic electrophiles. On heating di(hydroxymethyl)phenylphosphine or tri(hydroxymethyl)phosphine in a mixture of acetic acid and acetic anhydride, the corresponding acetates were obtained[6,134]. The reaction of di(α-hydroxyalkyl)-phenylphosphines with aldehydes leads to the formation of 1,3,5-dioxaphosphorinanes[95]. When tri(hydroxymethyl)-phosphine was heated with trimethyl orthoformate or trimethyl orthoacetate, trioxaphosphabicyclo[2.2.2]octane derivatives were obtained[164,165].

Organoelemental electrophiles can also react via the functional group. Tri(hydroxymethyl)phosphine[166,167] and alkyldi(hydroxyalkyl)phosphines[168] have been silylated. Chlorotriethylsilane and hexamethyldisilazane can be used instead of chlorotrimethylsilane. The employment of dichlorodimethylsilane and dimethoxydimethylsilane leads to the formation of 1,3,2,5-dioxasilaphosphorinanes. In the former case the reaction takes place in ether in the presence of triethylamine and in the latter on refluxing in toluene in the presence of sodium methoxide[169]:



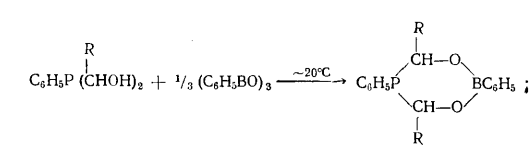
R=CH_3, C_2H_5, C_3H_7, C_6H_5, $CH(CH_3)_2$.

2,6,7-Trioxa-1,4-diphosphabicyclo[2.2.2]octane[170] and its arsenic and silicon analogues[171,172] have been obtained by the reaction of tri(hydroxymethyl)phosphine with trimethyl phosphite, trimethyl arsenite, and trichloromethylsilane. The reactions of tri(α-hydroxy-β,β,β-trichloroethyl)-phosphine with PCl_3, $AsCl_3$, and $C_6H_5SiCl_3$ in the presence of triethylamine lead to the formation of bicyclic compounds[173]:



Di(β-hydroxyethyl)phenylphosphine reacts with dichloromethylphosphine to form 1,3-dioxa-2,6-diphosphacyclooctane[174].

Organoelemental electrophiles of yet another type, which react under mild conditions with the functional group, are derivatives of boric acids. The isobutyl ester of diphenylborinic acid reacts with di(hydroxymethyl)phenylphosphine to form a *trans*-esterification product[175]. 1,3,2,5-Dioxaboraphosphorinanes have been obtained by the reaction with the diethyl ester or anhydride of phenylboronic acid[176,177]:

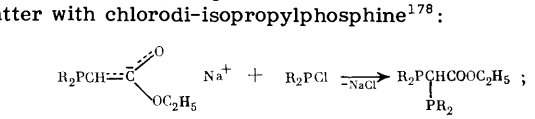


R=H, CH_3, iso-C_3H_7, C_6H_5 .

In contrast to phosphines with a mobile α-hydrogen atom, electrophilic substitution reactions without change in the coordination number of the phosphorus atom are characteristic of phosphines having a mobile β-hydrogen atom.

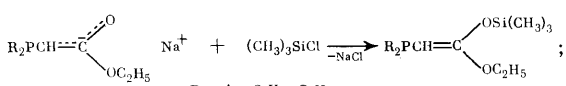
(c) Phosphine-containing Anions

Tertiary phosphines with functional-group substituents having a mobile α-hydrogen atom give rise to phosphine-containing carbanions on treatment with bases. These anions can react with chlorine-containing electrophiles both at the carbon atom and at the phosphorus atom. If the functional group contains the carbonyl moiety, the reaction can also proceed via the oxygen atom of the latter. Substitution at the carbon atom has been observed for the anions derived from phosphinoacetic esters on treatment of the latter with chlorodi-isopropylphosphine[178]:



R= iso-C_3H_7 .

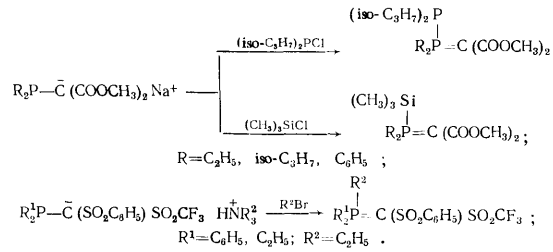
On the other hand, when the same compound was treated with chlorotrimethylsilane, the product of substitution at the oxygen atom was obtained[179]:



R= iso-C_3H_7, C_6H_5 .

Substitution at the phosphorus atom is characteristic of di(alkoxycarbonyl)methylphosphines and trifluoromethanesulphonylmethylphosphines. P–P– and P–Si– substituted ylides were obtained in the former case[180], while in the

latter case the products were alkyl-substituted phosphorus ylides[181]:



Electron-accepting substituents stabilise the $-\overset{\backslash}{P}-\overset{/}{C}R_2$ group; their accumulation increases the thermodynamic stability of the product of substitution at the phosphorus atom and drives the reaction towards its formation.

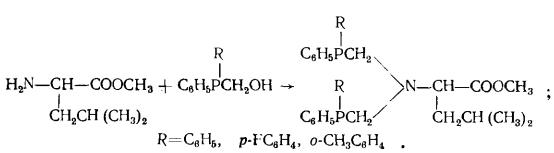
The study of the reactions with electrophiles has shown that there is an analogy in the behaviour of tertiary phosphines with a mobile hydrogen atom and the primary or secondary phosphines. Substitution at the phosphorus atom is also characteristic of the latter (examples of such reactions have been given in connection with the description of the methods of synthesis of tertiary phosphines with functional group substituents). The analogy is based on the ability of the phosphonium salts, obtained from all three types of compounds, to be stabilised by proton transfer to the negative centre of the electrophile. This method of stabilisation is related to that observed in the reactions of phosphorus(III) acids with electrophiles[182], which indicates considerable synthetic possibilities of the reactions examined. It must be emphasised that the phosphorus atom frequently does not prevent reactions with electrophiles also via the functional group.

2. Reactions with Nucleophiles

The carbon atom attached to the phosphorus atom is the electrophilic centre in the molecules of tertiary phosphines. The introduction of electron-accepting substituents should increase its reactivity. The departing groups can be both the substituent and the phosphino-group.

Nucleophilic substitution at the carbon atom has been most widely investigated for the hydroxy- and aminomethyl derivatives of phosphines. The nucleophiles employed have been primary, secondary, and tertiary amines. Various linear and cyclic products have been obtained.

The reactions of hydroxyalkylphosphines with primary and secondary amines proceed with the evolution of heat and lead to products of the substitution of the hydroxy-groups by amino-groups. Bis(diethylaminomethyl)phenylphosphine has been obtained from di(hydroxymethyl)phenylphosphine and diethylamine[183]. On treatment with hydroxymethyl derivatives of secondary phosphines, aminoacid esters have also given rise to derivatives of phosphorus-containing aminoacid[184]:



The reactions of the hydroxymethyl derivatives of secondary phosphines with ammonia and hydrazine have produced tri-(phosphinomethyl)amines, tri(phosphinomethyl)hydrazine, and tetra(phosphinomethyl)hydrazine[185]. The reactions of tri(hydroxymethyl)phosphine with secondary chiral amines and of hydroxymethyl derivatives of secondary amines with primary chiral amines proceeded analogously with formation of chiral tri(aminomethyl)phosphines and *N,N*-di(phosphinomethyl)amines respectively[186].

It has been shown that aminomethylphosphines can be obtained by heating acetoxymethylphosphines with secondary amines in methyl alcohol in the presence of alkali[187]:

$$R^1_nP(CH_2OCOCH_3)_{3-n} \xrightarrow{KOH} R^1_nP(CH_2OH)_{3\ n} \xrightarrow{R^2_2NH} R^1_nP(CH_2NR^2_2)_{3-n}\ ;$$

R^1=CH_2OH, C_2H_5, C_4H_9; R^2=CH_3, C_2H_5, C_3H_7, iso-C_4H_9; n=0—2 .

β-Hydroxyethylphosphines react with amines under the same conditions as hydroxymethylphosphines. When secondary amines are added to alkyldi(β-hydroxyalkyl)phosphines, an exothermic reaction is observed with formation of alkyldi(β-dialkylaminoalkyl)phosphines[188]:

$$R^1P(CH_2\underset{R^2}{C}HOH)_2 + 2R^3_2NH \rightarrow R^1P(CH_2\underset{R^2}{C}HNR^3_2)_2 + 2H_2O\ ;$$

R^1=CH_3, C_2H_5, C_3H_7, C_4H_9; R^2=H, CH_3; R^3=C_2H_5, C_4H_9 .

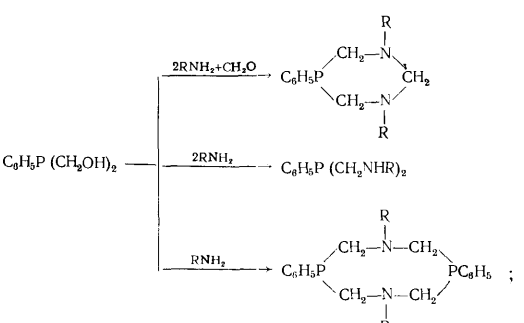
Monomeric products have been obtained by the reaction of tri(hydroxymethyl)phosphine with mono- or di-substituted ureas[189]:

$$3R^1R^2NCONH_2 + P(CH_2OH)_3 \rightarrow (R^1R^2NCONHCH_2)_3P{=}O\ ;$$

R^1=CH_3, C_2H_5, $CH_3(CH_2)_{11}$, $(CH_3)_3C$, C_6H_5; R^2=H, C_6H_5 .

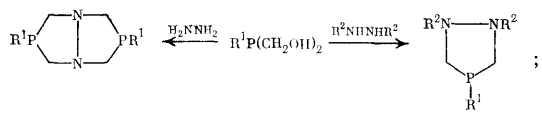
The oxidation of the product is attributed to the presence of formaldehyde in the reaction mixture.

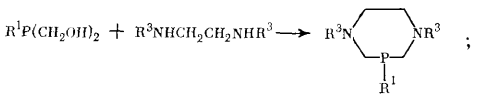
The reactions of di(hydroxymethyl)phenylphosphine with primary aromatic amines and benzylamine have attracted attention. They have been carried out in a solvent or in its absence, in the presence or absence of paraformaldehyde, and with different reactant ratios[190–192]. In all cases the reaction took place with evolution of heat. The structure of the *N,N*-disubstituted 5-phenyl-1,3,5-diazaphosphorinane was attributed to the product obtained in the presence of paraformaldehyde and two moles of the amine, while the products obtained in the absence of paraformaldehyde and in the presence of two and one moles of the amine were assumed to have the structure of *N,N*-disubstituted di(aminomethyl)phenylphosphines and 3,7-diphenyl-1,5-diaza-3,7-diphosphacyclo-octanes respectively:



The reactions of di(hydroxymethyl)phenylphosphine with boric acid esters took place analogously[193–197]. 1,5-Diaza-3,7-diphosphacyclo-octanes have also been obtained from diols containing aliphatic substituents at the phosphorus atom and a wide range of amines, including aliphatic amines[198].

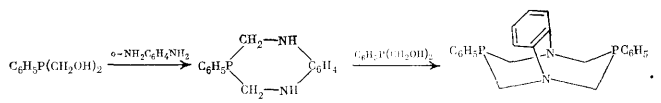
The reactions of di(hydroxymethyl)phosphines with hydrazine, substituted hydrazines, and ethylenediamine under the same conditions led to the formation of new heterocycles[199,200]:





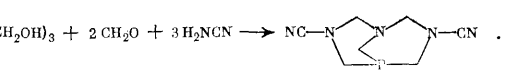
$R^1 = C_6H_5$, cyclo-C_6H_{11}, CH_3, C_2H_5; $R^2 = CH_3$, iso-C_3H_7; $R^3 = C_6H_5CHCH_3$.

o-Phenylenediamine reacts with di(hydroxymethyl)phenylphosphine only on heating and the products are 3-phenyl-6,7-benzo-1,5-diaza-3-phosphepane and 3,7-diphenyl-9,10-benzo-1,5-diaza-3,7-diphosphabicyclo[3.3.2]decane[201]:



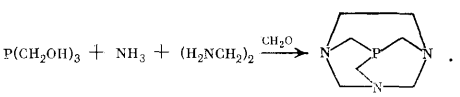
For a 1:1 reactant ratio, the product of the first stage of the reaction is obtained.

3,7-Dicyano-3,5,7-triaza-1-phosphabicyclo[3.3.1]nonane, which is capable of being oxidised and of combining with methyl iodide at the phosphorus atom, has been obtained by the reaction of tri(hydroxymethyl)phosphine with formaldehyde and cyanamide in the presence of phosphoric acid[202,203]:

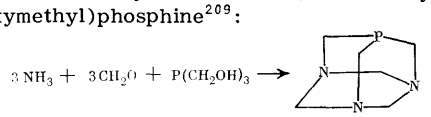


The reaction of tri(hydroxymethyl)phosphine with hexamethylenetetramine and formaldehyde (in portions of 1:1:4) has led to 1,3,5-triaza-7-phospha-adamantane[204,205]. This compound combines with methyl iodide and picric acid via one of the nitrogen atoms[206,207].

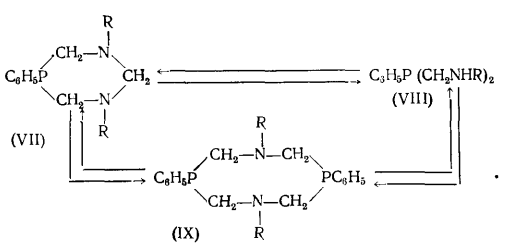
The synthesis of the next member of this series has been described[208]. Triazaphosphahomoadamantane is formed when ethylenediamine and ammonia react with tri(hydroxymethyl)phosphine in an excess of formaldehyde:



In contrast to triazaphospha-adamantane, it does not react with methyl iodide. 1,3,5-Triaza-7-phospha-adamantane is also obtained directly from ammonia, formaldehyde, and tri(hydroxymethyl)phosphine[209]:

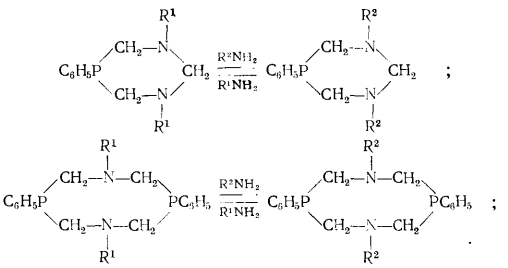


Not only the hydroxy-groups but also the amino-groups of tertiary phosphines with functional-group substituents readily undergo nucleophilic substitution. Thus the following interconversions of the aminomethyl derivatives of phenylphosphine have been demonstrated[210]:



Compounds (VII) and (IX) are converted into compound (VIII by amines. Diazadiphosphacyclo-octane (IX) can be obtained from compounds (VII) and (VIII) by the elimination of azomethines or amines respectively. The addition of azomethines to compounds (VIII) and (IX) gives rise to compound (VII). These reactions constitute nucleophilic substitution of one amino-group by another and proceed under fairly mild conditions.

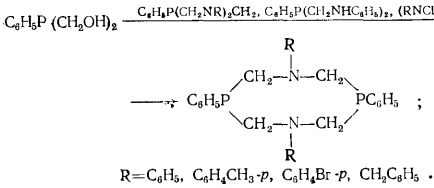
The substitution of one amino-group by another is also possible without alteration of the molecular skeleton[211]:



$R^1 = C_6H_5$; $R^2 = C_6H_4CH_3$-*p* .

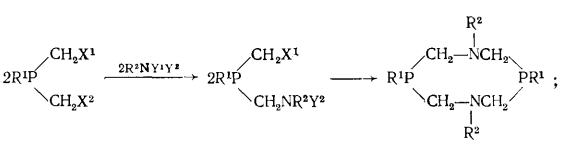
The interconversions are reversible; the direction of the reaction is determined by the conditions and the solubilities of the substances.

The hydroxy-group can be substituted by the amino-group on treatment not only with primary and secondary amines but also with triazanes or aminomethyl derivatives of phosphines. Thus di(hydroxymethyl)phenylphosphine and its borate esters give rise to 1,5-diaza-3,7-diphospha-cyclo-octanes on reaction with both primary amines and with 1,3,5-triphenyl-1,3,5-triazane, di(anilinomethyl)phenylphosphine, or 5-phenyl-1,3,5-diazaphosphorinanes[212]:



R=C_6H_5, $C_6H_4CH_3$-*p*, C_6H_4Br-*p*, $CH_2C_6H_5$.

The numerous methods of synthesis of 1,5-diaza-3,7-diphosphacyclo-octanes can be reduced to a single scheme[212]:



R^1 and R^2 — alkyls, aryls; $Y^1 = Y^2 = H$; $Y^1 = H$, $Y^2 = CH_2P$ (R) CH_2NHR; $X^1 = X^2 = OH$; $X^1 = OH$, $X^2 = OB(C_6H_5)_2$; $Y^1Y^2 = CH_2NRCH_2NRCH_2$, $X^1X^2 = OB(C_6H_5)O$, $NRCH_2NR$; $Y^1Y^2 = CH_2PRCH_2NRCH_2$, $X^1 = X^2 = NHR$.

The formation and transamination reactions and interconversions of the aminomethyl derivatives of phosphines, which constitute nucleophilic substitution at the carbon atom of the P–C–O or P–C–N fragment, proceed under milder conditions than the analogous reactions of alcohols, amines, and their derivatives. This is due to the involvement of the phosphino-group in intramolecular interactions. Examination of steric effects shows that the electron density in the P–C–O system is displaced towards the oxygen atom, while in the P–C–N system it is displaced towards the phosphorus atom. The transfer of electron density facilitates nucleophilic attack. In the former case the departing group is

the phosphino-group while in the latter it is the amino-group. The rupture of the P–C bond has been postulated in the reactions of di(hydroxyalkyl)phosphine oxides with amines[213].

The interactions of hydroxy- and amino-methylphosphines with nucleophiles have been fairly thoroughly investigated. Examples of such reactions for other tertiary phosphines with functional-group substituents are rarer. Tri(ethylchloromethyl)-phosphine is converted into tri(ethylthio)-phosphine on treatment with ethanethiol or sodium ethanethiolate[70]:

$$P(CH_2Cl)_3 \xrightarrow{3C_2H_5SH} P(CH_2SC_2H_5)_3 .$$

The addition of primary and secondary amines to diphenylvinylphosphine has been described[214]:

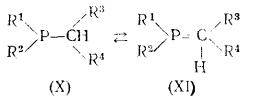
$$(C_6H_5)_2PCH_2CH_2NR_2 \xleftarrow{R_2NH} (C_6H_5)_2PCH=CH_2 \xrightarrow{+RNH_2} RN(CH_2CH_2P(C_6H_5)_2)_2 ;$$

$R = C_6H_5,\ C_2H_5$.

The amine attacks the β-position relative to the phosphorus atom.

3. Tautomerism

Prototropic tautomerism is possible for tertiary phosphines with functional-group substituents having a mobile hydrogen atom in the α-position. If centres capable of stabilising the proton are absent from the functional group, diad phosphorus-carbon tautomerism takes place:

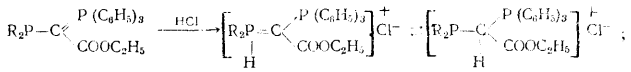


(X) (XI)

In the presence of such centres, other types of tautomerism cannot be excluded. The possibility of tautomerism depends mainly on the substituents at the carbon and phosphorus atoms.

The study of various tertiary phosphines has shown that, in the presence of alkyl and aryl substituents at the carbon atom, they exist in form (X). The stabilisation of the ylide form requires the introduction of strongly electron-accepting substituents such as the triphenylphosphonium, alkoxycarbonyl, and sulphonyl groups.

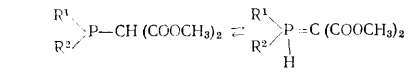
The presence of two triphenylphosphonium groups fully displaces the equilibrium towards form (XI). In the presence of butyl substituents at the phosphorus atom, the ylide has been isolated in a crystalline state[215,216]. The dependence of the equilibrium position on the substituents at the phosphorus atom has been observed for compounds containing the triphenylphosphonium and alkoxycarbonyl groups[217,218]:



$R = C_4H_9,\ C_6H_5$.

The butyl substituent stabilise the ylide formed. The replacement of butyl by phenyl leads to the establishment of a mobile tautomeric equilibrium and the relative contents of the different forms in solution depend on the temperature and the polarity of the medium. Only form (X) exists in trifluoroacetic acid. The substitution of the alkoxycarbonyl group by the tosyl group displaces the equilibrium towards the ylide form[219].

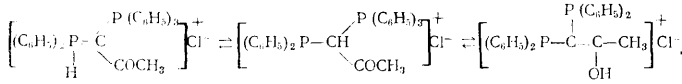
The occurrence of the diad phosphorus–carbon tautomerism has also been demonstrated for dialkyl(dimethoxycarbonylmethyl)phosphines[220–223]:



$R^1 = t\text{-}C_4H_9,\ R^2 = iso\text{-}C_3H_7,\ s\text{-}C_4H_9,\ (CH_3)_3SiCH_2,\ C_6H_5,$
$iso\text{-}C_4H_9;\ R^1 = R^2 = iso\text{-}C_4H_9,\ C_6H_5$

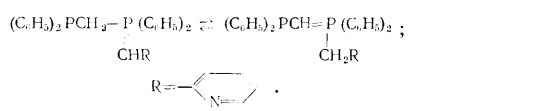
When R^1 = iso-C_4H_9 and R^3 = iso-C_3H_7, s-C_4H_9, or $(CH_3)_3SiCH_2$, the compounds are in the ylide form in the crystalline state. On fusion, a considerable proportion of the ylide is converted into a tertiary phosphine, which again crystallises in the ylide form. In solution, the compounds exist as tautomeric mixtures of forms (X) and (XI). The equilibrium position depends on the temperature, the nature of the solvent, the concentration, and the character of the substituents at the phosphorus atom. Heating shifts the equilibrium towards form (X). Bulky substituents stabilise the ylide form and in terms of their influence can be arranged in the following sequence: C_5H_9 < iso-C_4H_9 < iso-C_3H_7 < s-C_4H_9 < $(CH_3)_3SiCH_2$ < t-C_5H_9.

The substituted tertiary phosphines examined above exhibit only the diad phosphorus–carbon tautomerism despite the presence of carbonyl groups. The tetrad phosphorus–carbon tautomerism has been observed on substitution of the alkoxycarbonyl group in these compounds by the acetyl group[217,218]:



This type of tautomerism includes the diad phosphorus–carbon tautomerism and the keto-enol tautomerism.

The introduction of an ylide group as a substituent into the molecule of a tertiary phosphine results in the transfer of the mobile hydrogen atom to this group. The process can be both reversible and irreversible[224]:



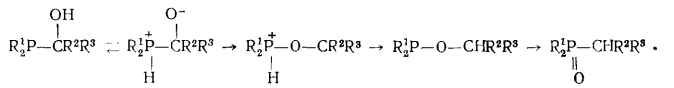
Proton transfer to the phosphorus atom has been observed in acetonyldiphenylphosphine under the influence of tin tetrachloride[225]:

The observation of the prototropic diad phosphorus–carbon tautomerism emphasises the powerful influence of substituents on the properties of tertiary phosphines.

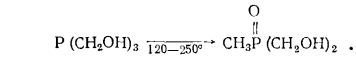
4. Rearrangements

The lability of the P–C bond and the close proximity in space of the substituents at the phosphorus atom in tertiary phosphines with function-group substituents can lead to rearrangements whose character depends on the nature of the solvents. The rearrangements of hydroxyalkylphosphines have been most thoroughly investigated. It has been suggested that the hydroxyalkylphosphine molecule is in equilibrium with the dipolar ion formed as a result of proton transfer to the phosphorus atom. This dipolar ion can rearrange to another dipolar ion containing the P–O–C group. The rearrangement is irreversible and the ion is stabilised by proton transfer to the carbon atom with formation of a phosphinite; the subsequent isomerisation yields

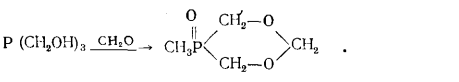
the compounds most stable in the given system—tertiary phosphine oxides[226]:



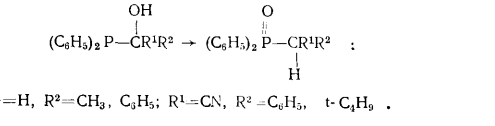
Tri-(hydroxymethyl)phosphine isomerises on heating to di(hydroxymethyl)methylphosphine oxide[227-231]:



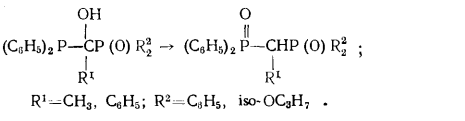
When paraformaldehyde is added, 5-methyl-5-oxo-1,3,5-dioxophosphorinane is formed[232]:



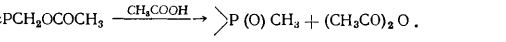
In the case of the hydroxyalkyl derivatives of diphenylphosphine, the rearrangement was observed for different C-substituted compounds[226,233]:



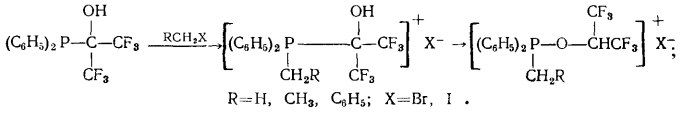
Replacement of the phenyl group at the phosphorus atom by the ethyl group does not affect the possibility of this rearrangement[226]. α-Phosphorus-substituted phosphinomethanols also give rise to rearrangement products on heating[234,235]:



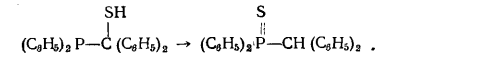
The isomerisation of hydroxyalkylphosphines to tertiary phosphine oxides can occur under the influence of acids and bases[233,236]. Acetoxymethylphosphines rearrange in an acid medium[237,238]:



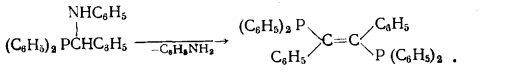
In the examples quoted above the oxygen atom is transferred to the phosphorus atom and the reaction cannot be arrested at the phosphinite formation stage. Phosphonium compounds with the P–O–C group have been obtained by treating with alkyl halides hydroxyalkylphosphines having trifluoromethyl groups at the carbon atom[236]:



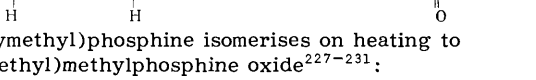
The study of mercaptoalkylphosphines has shown that they too are capable of rearranging to tertiary phosphine sulphides. The mechanisms of the rearrangements are apparently analogous. This follows from the conversion of α-mercaptobenzhydryldiphenylphosphine in benzhydryldiphenylphosphine sulphide[15]:



The organonitrogen analogues of hydroxyalkylphosphines are converted into 1,2-diphosphinoethylenes. This is accompanied by the formation of the corresponding arylamines[239]:

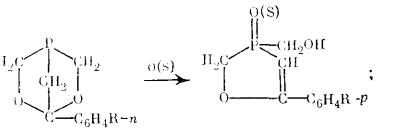


The rearrangement of α-halogenophosphines, formed on interaction of phosphinous acid chlorides with α-halogenomethyl sulphones in the presence of triethylamine or the sodio-derivatives of α-halogenodi(benzenesulphonyl)-methanes, to *P*-halogenoylides has been described[240,241]:



It has been suggested that the rearrangement involves the concerted bimolecular transfer of a halogen atom via a six-membered transition state. This reaction has also been examined in other studies[242,243]. α-Halogenophosphines with alkyl substituents at the carbon atom are stable[244].

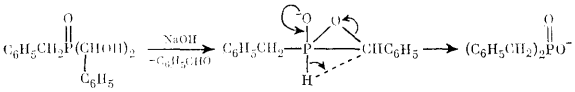
Many rearrangements are known for substituted phosphines, which can proceed under the conditions of oxidation or sulphur addition reactions. 4-Aryl-1-phospha-3,5-dioxabicyclo[2.2.1]heptane gives rise on oxidation or addition of sulphur to the oxide or sulphide of 4-aryl-1-hydroxymethyl-1-phospha-3-oxacyclopent-4-ene respectively[245,246]:



The migration of the phenyl group from the phosphorus atom to the carbon atom has been observed in the reactions of ferrocenyldiphenylphosphines, leading to the formation of phosphonium betaines and binylphosphonium salts[247]:



When benzyldi(α-hydroxybenzyl)phosphine oxide is heated with an equimolar amount of alkali in benzene, the sodium salt of dibenzylphosphinic acid is formed in an almost quantitative yield[248]:



Hydride transfer from the phosphorus atom to the carbon atom in the intermediate anion has been postulated in this reaction.

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Thus the introduction of substituents alters significantly the properties of tertiary phosphines; new pathways to the decomposition of the phosphonium compound appear and reactions with nucleophiles as well as rearrangements become characteristic of these compounds. The high and many-sided reactivity of tertiary phosphines with functional-group substituents together with the existence of a large number of convenient methods of their synthesis makes it useful to investigate this class of compounds.

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Arbuzov Institute of Organic
and Physical Chemistry,
Kazan Branch of the USSR Academy
of Sciences, Kazan

Translated from *Uspekhi Khimii*, 53, 651-688 (1984) U.D.C. 547.333

Advances in the Chemistry of Enamines

V.G.Granik

The review surveys the results of studies on the physicochemical and chemical properties of enamines. Special attention has been devoted to the employment of enamines in the synthesis of various heterocyclic systems.
The bibliography includes 236 references.

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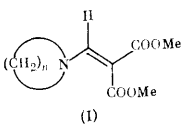
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I. INTRODUCTION

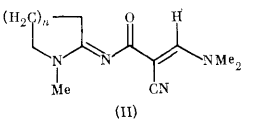
The chemistry of enamines is at present one of the most vigorously developing fields of organic synthesis and the number of publications concerning the properties and reactions of these compounds continuously increases. Because of this and despite a whole series of reviews dealing with various aspects of the chemistry of enamines and related compounds[1-14], it is useful to survey the extensive data published in recent years (mainly in 1977–1982), obtained in the study of various types of enamine systems. The present review does not deal specially with publications describing the methods of synthesis of various enamines since fundamentally new data have not become available in this field and the known methods of synthesis of enamines have already been discussed in detail[1]. As a rule, studies on the chemistry of different classes of enamines which have been included in the reviews mentioned above are also not dealt with.

II. STRUCTURAL STUDIES, PROTONATION, AND HYDROLYSIS OF ENAMINES

The spectroscopic studies on enamines published in recent years were devoted mainly to stereochemical aspects of these compounds[15-24]. The study of the hindered rotation about the enamine C–C bond in enaminoesters of type (I) has shown that the main factors which determine the kinetic and thermodynamic parameters of this process are the degree of conjugation of the nitrogen atom with the double bond in the ground state and the extent of the non-bonding interaction between the amino-fragment and the *cis*-COOMe group which is non-planar in the ground state[15]:



(I)



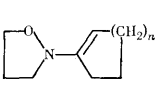
(II)

Another problem, that of hindered rotation about the single N–C bond, was also investigated in the above study[15]. An analogous process has been discovered and investigated for enaminoacylamidines (II)[16]. The study of the ^{13}C NMR spectra of a large group of enamines[17-19] established that the chemical shifts of the β-carbon atom in these compounds are extremely sensitive to the steric factor[17]. On the other hand, if this factor does not vary in various compounds, the chemical shift of the β-carbon atom serves as a characteristic of the electron density. In cyclic enamines the electron density and hence the degree of conjugation of the nitrogen atom with the C–C bond is highest for the pyrrolidine enamines[18]:

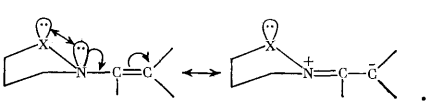


(III)

The study of the ^{15}N NMR spectra led to the conclusion that the nitrogen atom in enamines has the sp^2 configuration[19]. On the other hand, photoelectron spectroscopic data indicate a pyramidal configuration of the nitrogen in enamines, in contrast to the corresponding radical-cation where the configuration is planar[20]. It is extremely interesting that the ^{15}N NMR spectra are not correlated with ^{1}H NMR and ^{13}C NMR spectroscopic data in the sense that the chemical shifts in ^{15}N NMR are almost indistinguishable for pyrrolidine and piperidine enamines. The authors attribute this inconsistency to the fact that in their view a change in electron density at the nitrogen atom is not in this instance a decisive characteristic of the chemical shift of this atom[21]. One must agree with this view, since extensive chemical and physicochemical data leave no doubt at the present time that the degree of the "enamine" conjugation in the pyrrolidine enamines [III, X = $(CH_2)_4$] is greater than in the piperidine and morpholine analogues. This is also supported by the results of the X-ray diffraction analysis of enamines[22], which indicate a higher degree of planarity of the enamine fragment in the pyrrolidine enamines than in the piperidine and morpholine analogues. The literature concerned with the differences between the $p\pi$ conjugations in enamines of type (III) has been analysed in detail[23]; the authors attempted to increase the extent of this conjugation still further by replacing the pyrrolidine ring by the tetrahydroisoxazole ring:



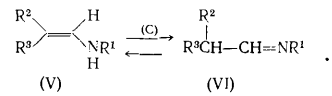
(IV)



(A) (B)

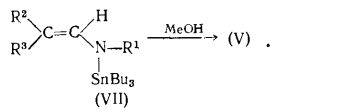
The idea was that the repulsion of the neighbouring free electron pairs leads to an increase of the extent of the enamine conjugations (A) ↔ (B). However, it has been established both spectroscopically (^{1}H and ^{13}C NMR) and chemically (reaction with acrylonitrile) that in enamines (IV) the

degree of $p\pi$ conjugation and hence the reactivity with respect to electrophiles are lower owing to the negative inductive effect of the oxygen atom. Among the studies devoted to the imine–enamine tautomerism[25–27], we shall note those dealing with the secondary enamines (V) lacking β-electron-accepting substituents[25]:



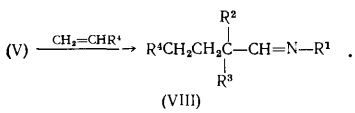
(V) (VI)

Such enamines are usually unstable and the equilibrium (C) is displaced towards the corresponding imines (VI). However, the authors[28] were able to isolate the kinetic product (V) by the methanolysis of the organometallic derivatives (VII) in the presence of a deficiency of methanol:



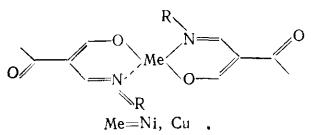
(VII)

It is known that the reactions of the imine (VI) with unsaturated compounds, which proceed via equilibrium (C), require prolonged heating (for 24 h at 80 °C) and in many cases do not occur at all. On the other hand, when the pure enamine (V) is used in such processes, a rapid exothermic reaction is observed even at 0 °C with formation of a substituted imine (VIII):



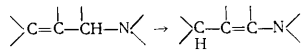
(VIII)

The formation of extremely stable copper(II) and nickel(II) complexes of enaminoketones and enaminoamides is accompanied by the conversion of the enaminocarbonyl compounds into the iminoenol form[28]:

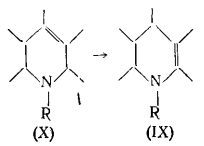


Me=Ni, Cu .

The communication of Martinez and Joule[29], which includes extensive literature and experimental data on the allylamine → enamine isomerisation, was devoted to the problem of the stability of the enamine structure:



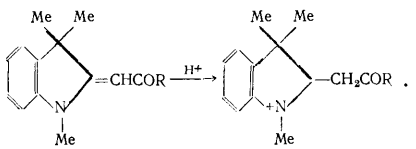
It was established that the enamines 2-piperideines (IX) are thermodynamically more stable than 3-piperideines (X) and that isomerisation takes place in the presence of bases:



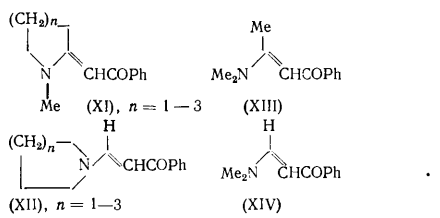
(X) (IX)

The energy gain is due to the $p\pi$ conjugation and has been estimated as 2.5 kcal mol^{-1}.

The problem of the protonation and hydrolysis of enamines occupies a notable place in their chemistry[1,11]. Investigations of the traditional type, dealing with the study of the insufficiently clear problems of the mechanism of the hydrolysis of enamines of various types and the factors determining the particular site of the protonation of these compounds, and studies in which the protonation of enamines is used as an intermediate stage for the attainment of synthetic aims have been published in recent years. Among the investigations of the first kind, we may point to those dealing with the protonation of enamines in the gas phase[20,31], where it was shown that in cases where there is no steric inhibition of the $p\pi$ conjugation in enamines the protonation proceeds via the β-carbon atom. A number of studies have been devoted to the problem of the protonation of enaminoketones, but, whereas Kozerski[32] established with the aid of ^{13}C NMR what is in general an unusual fact[1,11], namely the *O*-protonation of these compounds, Bailey et al.[33] indicate a rare instance† of the protonation of enaminoketones at a carbon atom:



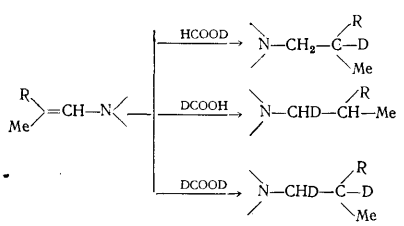
The study of the basicity and ^{1}H NMR spectra of the cyclic enaminoketones (XI) and (XII) and their acyclic analogues (XIII) and (XIV) showed that compounds (XI) and (XIII) are more basic approximately by 2–3 orders of magnitude than compounds (XII) and (XIV), which is caused by the different sites of protonation [compounds (XI) and (XIII) are protonated at the β-carbon atom, while compounds (XII) and (XIV) are protonated at the oxygen and nitrogen atoms[35]]:



(XI), $n = 1-3$ (XIII)

(XII), $n = 1-3$ (XIV)

The use of deuterated acids as protonating agents made it possible to obtain deuterated compounds from the enamines[36]:

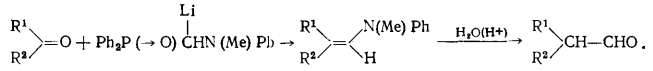


The mechanism of the hydrolysis of enaminoketones has been investigated at different pH of the solution[37] and the stages determining the rate of the overall process have been established. For the enamines RNHC(Me)=CHCOMe (R = alkyl) these stages involve the addition of water (at pH > 2) and the decomposition of the carbinolamine (at pH < 2). When R = aryl, hydration is the slow stage in all the media investigated. The kinetics of the hydrolysis of the enaminoketones (XI)–(XIV) have been investigated in a number of

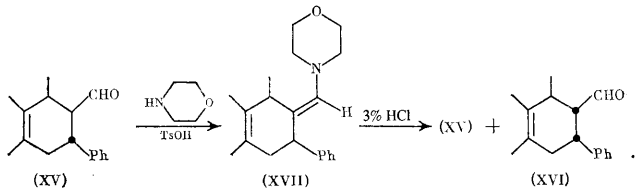
† Bailey et al.[33] state that this is the first instance of the *C*-protonation of enaminoketones. In fact this is not the case—the *C*-protonation of enaminoketones had been observed for the first time much earlier[34].

studies[38,39]. It has been shown that the rate of C-protonation limits the rate of hydrolysis at pH 3–6 and that the rate and direction of the process depend significantly on the ring size#.

The protonation of enamines with formation of immonium cations followed by their hydrolysis made it possible to develop a series of interesting synthetic methods. Thus enamines are intermediates in a new synthesis of homologous aldehydes from ketones[41]:

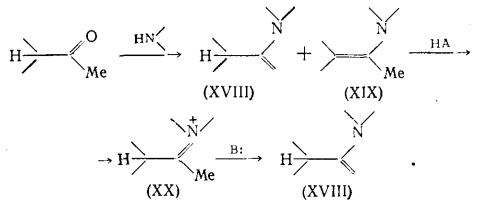


The formation of the *cis*-isomer (XVI) from the *trans*-compound (XV) was required[42]. The usual isomerisation procedures were unsuccessful but treatment of the intermediate enamine (XVII) with hydrochloric acid leads to a mixture of isomers containing 52–56% of the *cis*-compound (XVI):

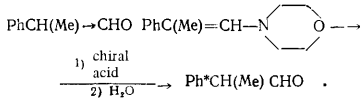


The required isomer (XVI) was isolated from this mixture by crystallisation[42].

The conversion of enamines into immonium salts has been used for the selective synthesis of enamines with a terminal double bond[43]. It has been shown[43] that, although treatment of ketones with amines gives rise to a mixture of the enamines (XVIII) and (XIX), the conversion of this mixture into the salt (XX) followed by treatment with t-butylamine or secondary amines leads to the selective formation of the enamine (XVIII):



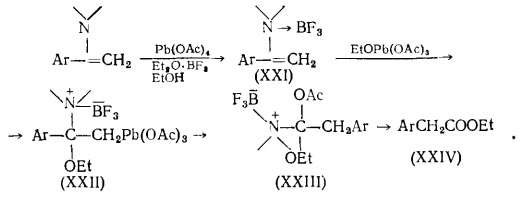
The intermediate synthesis of immonium salts also serves as a basis for the preparation of optically active carbonyl compounds[44–46]. For example, it has been established that, when enamines are protonated by chiral acids with subsequent hydrolysis, the initial carbonyl compounds undergo "deracemisation" and the degree of formation of optically active aldehyde and ketones depends on the configuration of the enamine and the structure of the optically active acid[45]:



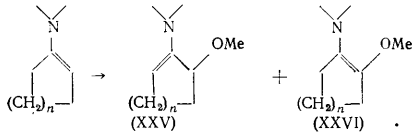
The dependence of various properties, including the protonation and hydrolysis, of enamines on ring size has been discussed in a review[40].

III. OXIDATION AND REDUCTION OF ENAMINES

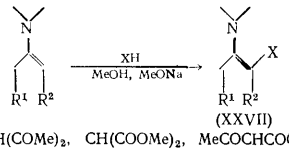
The number of studies devoted to the oxidation of enamines of different types is relatively small. It has been established that, when enamines are oxidised by lead tetra-acetate in the presence of boron trifluoride etherate[47], a rearrangement involving the formation of the adducts (XXI)–(XXIII) with BF_3 takes place and results in the formation of arylacetic acid esters (XXIV):



The anodic oxidation of enamines in methanol leads to the methoxyenamines (XXV) and (XXVI)[48]:

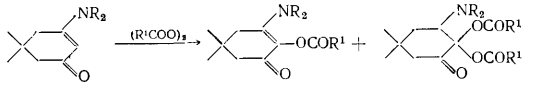


Substituted enamines of type (XXVII) have been obtained in the presence of organic anions[49]:

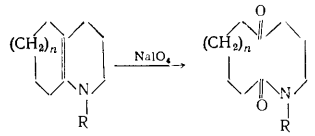


X =CH(COMe)$_2$, CH(COOMe)$_2$, MeCOCHCOOMe .

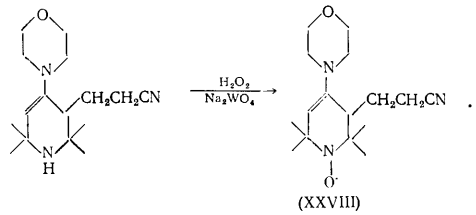
When alicyclic enaminoketones interact with diacyl peroxides, acyloxylation products are formed[50]:



The oxidation of bicyclic enamines is one of the ways of synthesising macrocyclic compounds[51]:

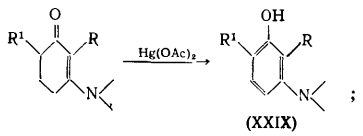


The nitroxy-radicals (XXVIII) have been obtained by the oxidation of certain heterocyclic enamines[52]:

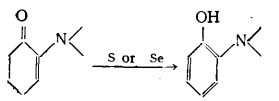


Enaminoketones can serve as the starting compounds in the synthesis of derivatives of *m*-aminophenol (XXIX) or *o*-aminophenol (XXX)—either the oxidation of enaminoketones[53] or

their dehydrogenation with sulphur or selenium[54] are used for such purposes:

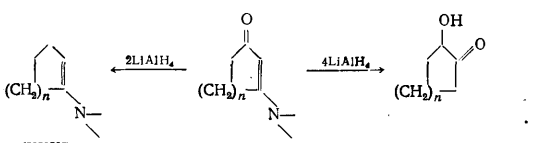


(XXIX)



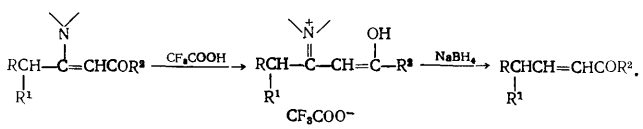
(XXX)

The reduction of enaminoketones with lithium tetrahydroaluminate was investigated in the same study[54] and it was established that, depending on the excess of the reductant, enamines or acyloins, (XXXI) and (XXXII) respectively, are formed:

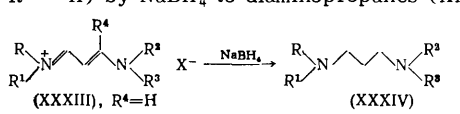


(XXXI) (XXXII)

A successful method of the reduction of enaminoketones to the corresponding unsaturated ketones was used by Nilsson[55]:

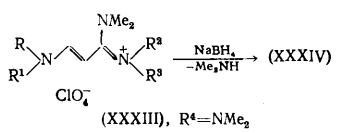


The reduction of enaminoketones by diborane to alkyl vinyl ketone derivatives[56] and the polarographic reduction of enaminoketones to the corresponding aminoalcohols[57] have also been described. Like enaminoketones, enaminoimines can be reduced in the form of the enaminoimmonium salts (XXXIII, $R^4 = H$) by $NaBH_4$ to diaminopropanes (XXXIV)[58]:



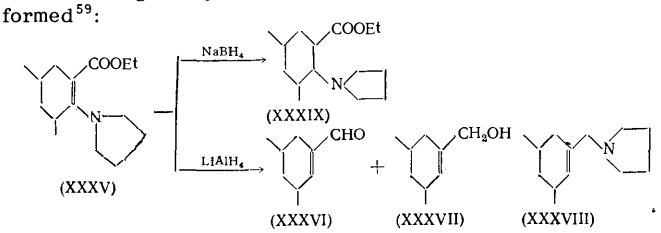
(XXXIII), R^4=H (XXXIV)

It is of interest that in the case of the salts of the enaminoamidines (XXXIII, $R^4 = NMe_2$) the reaction is accompanied by the elimination of dimethylamine[58]:



(XXXIII), R^4=NMe_2

In the reduction of the enaminoesters (XXXV) with lithium tetrahydroaluminate, a mixture of derivatives of unsaturated aldehydes (XXXVI), hydroxymethylalkenes (XXXVII), and aminomethylalkanes (XXXVIII) is formed[59]. The reaction of compound (XXXV) with sodium tetrahydroborate proceeds more unambiguously and the aminoesters (XXXIX) are formed[59]:



(XXXV) (XXXIX) (XXXVI) (XXXVII) (XXXVIII)

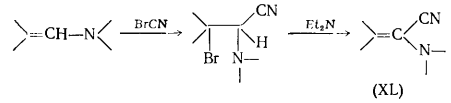
Orthophosphorous acid is an effective reagent for the reduction of enamines; saturated amines are formed in this case in high yields[60]. Finally, we may note a study[61] in which the asymmetric synthesis of β-aminoacids was achieved by the reduction of chiral enamines either catalytically over palladium or with $NaBH_3CN$:



In the former case (catalytic reduction) the process proceeds with retention of the configuration, while in the latter case the configuration is inverted[61].

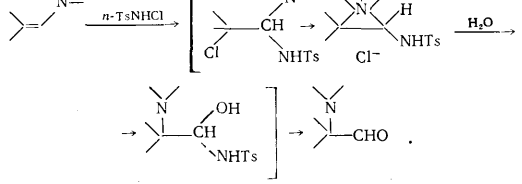
IV. ADDITION TO THE ENAMINE DOUBLE BOND, CYCLOADDITION, AND REARRANGEMENTS

The addition of bromocyanogen to the double bond of enamines with subsequent elimination of hydrogen bromide has been a convenient method of synthesis of α-cyanoenamines (XL)[62]:

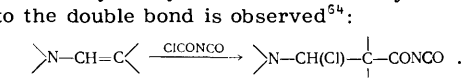


(XL)

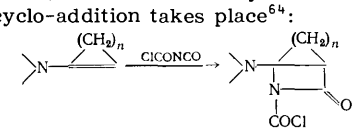
The reaction of enamines with chloramine-T is also accompanied by the initial addition of the latter to the C–C bond and ultimately leads to α-aminoaldehydes[63]:



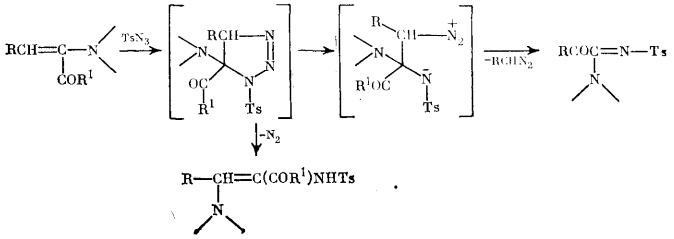
When chloroformyl isocyanate reacts with acyclic enamines, addition to the double bond is observed[54]:



On the other hand, on treatment of cyclic enamines with this reagent, 1,2-cyclo-addition takes place[64]:

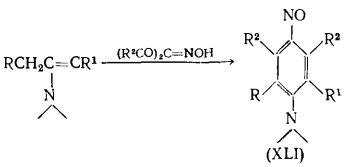


Cycloaddition reactions occur also in the interaction of enamines with aryl azides and arenesulphonyl azides[65–67]. For example, enamines having an α-keto-group react with sulphonyl azides in two ways[67]:



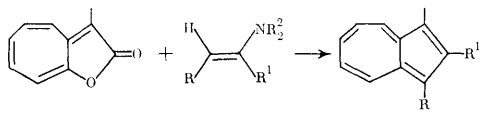
The interaction of enamines with diazoacetic ester, which also proceeds via a type of cycloaddition mechanism, leads to pyrazolines[68]. The reactions with enamines of α,α′-dibromoketones (with formation of cyclopentenones)[69], of unsaturated ketones (with formation of pyran derivatives)[70],

and of acetylenedicarboxylate ester (with formation of condensed cyclobutenes)[71] proceed via this same mechanism.
A new method of synthesis of nitrosoanilines (XLI) by the reaction of enamines with isonitroso-β-dicarbonyl compounds has been published recently[72]:



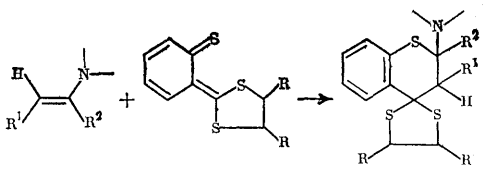
(XLI)

A number of studies have been devoted to the synthesis of azulenes (XLII) from bicyclic lactones (XLIII) and enamines[73–75]:

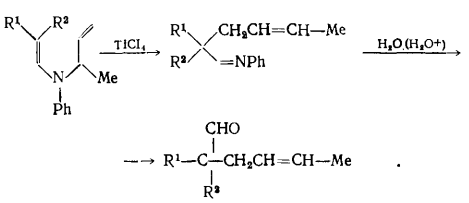


(XLIII) (XLII)

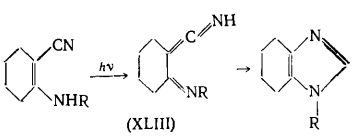
The reaction of enamines with *o*-thioquinone methide[76] results in the formation of [1:1]-adducts:



The reactions of enamines with thioacylketen thioacetals were described in the same communication[76]. In many instances the reactions of enamines are accompanied by rearrangements. It was mentioned above that, when enamines are oxidised in the presence of boron trifluoride etherate, a transformation of the type of the Favorskii rearrangement is observed[47]. In the presence of titanium tetrachloride enamines having substituents at the nitrogen atom with a terminal carbon–carbon double bond undergo the aza-Claisen arrangement[77]:

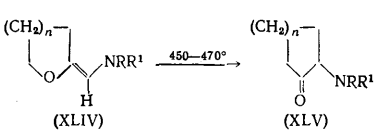


The photochemical rearrangement of enaminonitriles results in the formation of imidazole derivatives[78] with the aminoketimine (XLIII) as an intermediate[79]:



(XLIII)

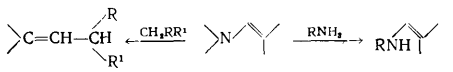
It has been established recently that enamines of type (XLIV) are converted at high temperature into the aminoketones (XLV) in high yields[80]:



(XLIV) (XLV)

V. THE REACTIONS OF ENAMINES WITH NUCLEOPHILES AND ELECTROPHILES

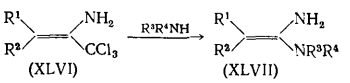
The reactions of enamines with nucleophiles which are most frequently used are those with various amines (transamination)[81–87] and with compounds having an active methylene unit[88]:



The kinetics of the transamination reactions of various enamines have been investigated[82,87]. In the study of the interaction of the enaminoketones MeCOCH=C(Me)NHR with phenylhydrazine, it was established[82] that the rate of the process depends on the character of the substituent (electron-donating groups accelerate the reaction) and the configuration of the initial enaminoketone (the *E* derivatives react more slowly than the *Z* derivatives). The rate-limiting stage of the reaction is *C*-protonation[82].

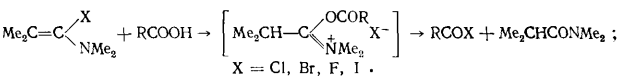
It has been shown[87] that the rate of transamination depends on the degree of delocalisation of the negative charge of the enamines by β-substituents and the possibility of the stabilisation of the transition state as a result of the formation of an intramolecular hydrogen bond. It was established that the rate of the process depends on the solvent—the rate of transamination in ethylene glycol is 40 times higher than in dimethylformamide.

In those cases where a readily removed group (for example a halogen) is attached to the β-carbon atom of the enamine, the reactions with nucleophiles are accompanied by the substitution of this group[89–91]. It is of interest that α-trichloromethyleneamines (XLVI) react with amines to form enediamines (XLVII), i.e. a reaction of the type of haloform cleavage takes place[90]:

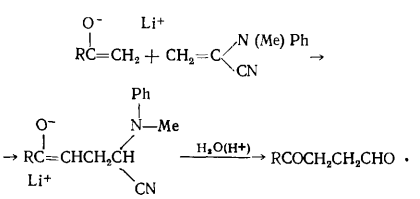


(XLVI) (XLVII)

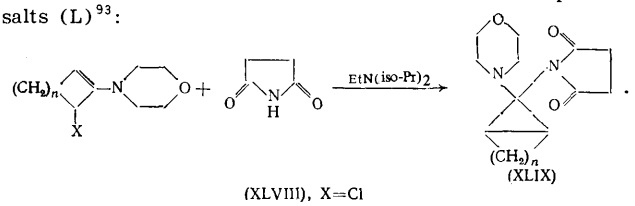
The reaction of α-halogenoamines with carboxylic acids constitutes a convenient method of synthesis of acid halides[91]:



The interaction of enamines with enolate anions is the basis of a new synthesis of 1,4-dicarbonyl compounds[92]:

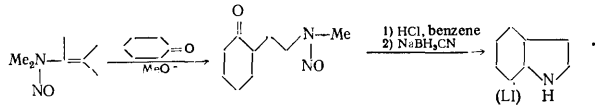


The succinimide anion reacts with chloroenamines (XLVIII) to form the bicyclic compounds (XLIX) having the *trans*-configuration. The corresponding *cis*-bicyclic compounds are formed when succinimide reacts with enaminosulphonium salts (L)[93]:

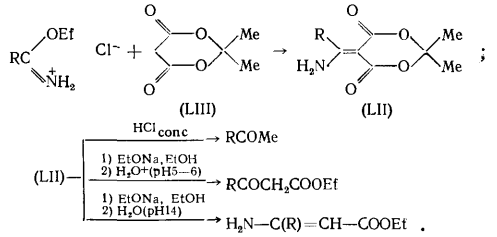


(XLVIII), X=Cl
(L), X=$Me_2\overset{+}{S}$ (anion—FSO_3^-)
(XLIX)

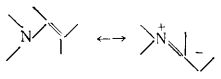
N-Nitrosoenamines are also capable of reacting with nucleophiles[94]. For example, perhydroindoles (LI) can be obtained as a result of such reactions:



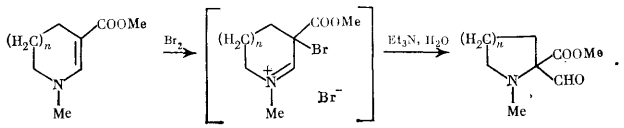
The enamines (LII), synthesised by the reaction of iminoesters or lactim-esters with Meldrum's acids (LIII), proved to be convenient intermediates for the preparation of β-monosubstituted enamines, β-dicarbonyl compounds, and substituted ketones[95–97]:



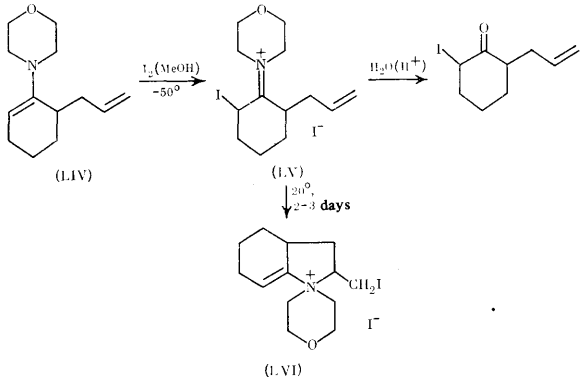
The interaction of enamines with electrophiles can proceed via two centres (in enaminoketones there is yet another centre—the oxygen atom): the nitrogen atom and the β-carbon atom:



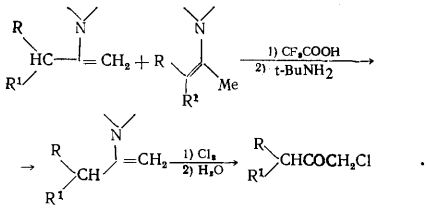
The halogenation of enamines has been studied in extremely great detail and usually proceeds via the β-carbon atom. Thus β-bromination is an intermediate stage in the synthesis of azacyclic aldehydes[98]:



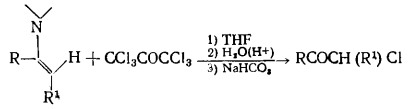
When the enamine (LIV) is iodinated at a low temperature, it is possible to isolate the intermediate immonium salt (LV), which is converted into the corresponding iodoketone on treatment with water and, on being kept at 20 °C, cyclises to an indolinium derivative (LVI)[99]:



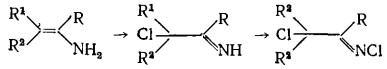
A new simple synthesis of halogenomethyl ketones[100] is based on the phenomenon already discussed (see above), according to which the treatment of immonium salts with bases leads to the selective formation of enamines with a terminal double bond:



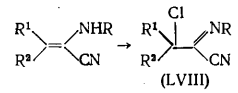
It has been established recently[101] that hexachloroacetone can be used as a chlorinating agent in the reaction with enamines at −78–0 °C in tetrahydrofuran (THF):



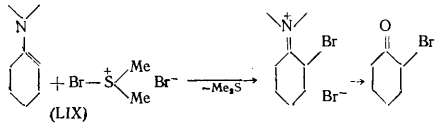
When β,β-disubstituted primary enamines are chlorinated, the reaction involves initially the β-carbon atom and then the nitrogen atom with formation of *N*,β-dichloro-derivatives (LVII)[102]:



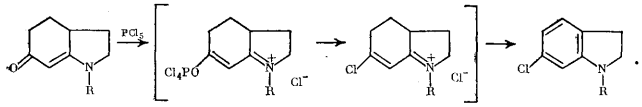
The C-chlorination of cyanoenamines by *N*-chlorosuccinimide[103] leads to α-halogenoimidoyl cyanides (LVIII):



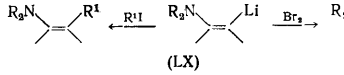
α-Bromoketones have been synthesised recently by the reaction of bromodimethylsulphonium bromide (LIX) with enamines and subsequent hydrolysis of the intermediate immonium bromides[104]:



The reactions of enaminoketones with reagents such as phosphoryl chloride or phosphorus pentachloride[105] proceed in accordance with the same principle as the reactions of amides with these compounds—there is initial electrophilic attack on the oxygen atom. In many instances the process is accompanied by aromatisation:

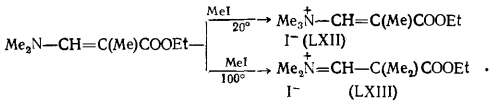


Finally, the introduction of the halogen atom into the "enamine" β-position can be achieved also via the lithioenamines (LX). In the study by Duhamel and Poirier[106] and others by the same workers[13,107,108], lithioenamines were introduced into reactions not only with the halogens but also with other electrophiles such as alkyl halides and aldehydes:

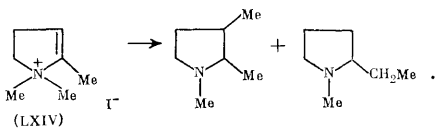


Studies of the alkylation reactions of enamines occupy a very notable place in their chemistry[107–124], much attention being devoted to factors which determine the site of attack by the

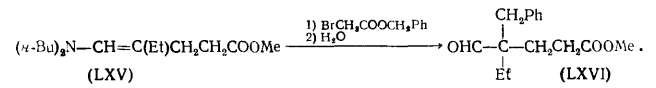
alkylating agent (*N*- or *C*-alkylation). The study of the alkylation of α-methyl-β-(*N*,*N*-dimethylamino)acrylic acid ester (LXI) by methyl iodide established[109] that the pathway followed in the process depends on the temperature—the enammonium salt (LXII) is formed at a low temperature, while the product at a high temperature is the immonium salt (LXIII):



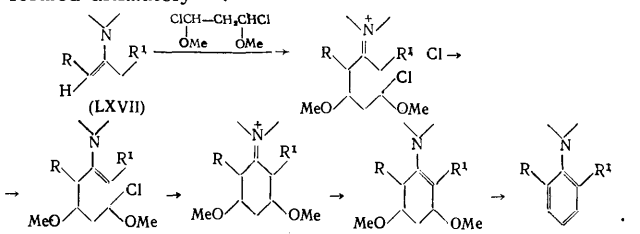
The question whether the β-*C*-alkylation of enamines is an independent process or whether the *N*-alkyl derivatives formed initially rearrange to the *C*-alkyl derivatives has been considered[112]. The enammonium salt (LXIV) was heated to 240 °C and the mixture reduced with formic acid was analysed by gas–liquid chromatography. It was established that, on heating, the *N*-methyl group migrates to the enamine carbon atoms:



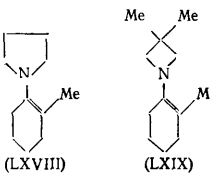
The authors[112] also showed that, when a mixture of enammonium salts is heated, the migrating *N*-alkyl substituents are distributed in both enamines formed, which indicates the intermolecular character of the N→C transfer of the alkyl substituent. An unusual β-*C*-alkylation has been described[113]. It was established that the interaction of the enamine (LXV) with benzyl α-bromoacetate leads to the β-benzylaldehyde (LXVI) (after hydrolysis) and not to the expected alkoxycarbonylmethyl derivative:



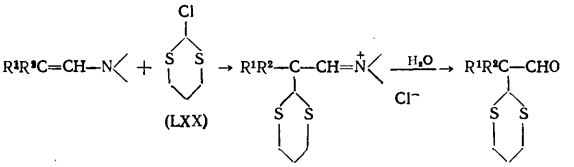
Regardless of the nature of the alkylating agent, the alkylation of *N*-monosubstituted-cyanoenamines proceeds at the N atom and the best results are obtained when triethyloxonium fluoroborate is used[114]. The same reagent has been employed successfully for the *O*-alkylation of enaminoamides[86] The reaction of the enamines (LXVII) with 1,3-dichloro-1,3-dimethoxypropane proceeds in an interesting manner—in this case double *C*-alkylation takes place and aniline derivatives are formed ultimately[115]:



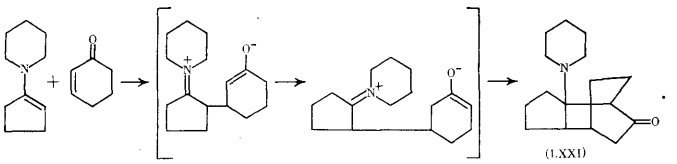
Comparison of pyrrolidine and azetidine enamines (LXVIII) and (LXIX) in reactions involving alkylation by methyl iodide[116] showed that the iodide is involved in *N*-alkylation to a greater extent:



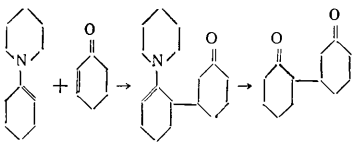
The alkylation of enamines by 2-chloro-1,3-dithian (LXX) has served as the basis of a new method of synthesis of malonodialdehyde with one protected aldehyde group[117]:



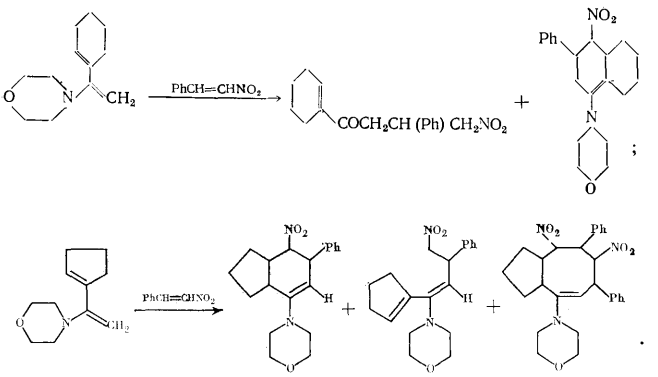
Compounds with an active double bond also readily alkylate enamines[118–122]. Thus the reaction of an enamine derived from cyclopentanone with cyclohexen-2-one results in the formation of compound (LXXI)[120]:



It is of interest that the reaction of the enamine derived from cyclohexanone proceeds differently[120]:

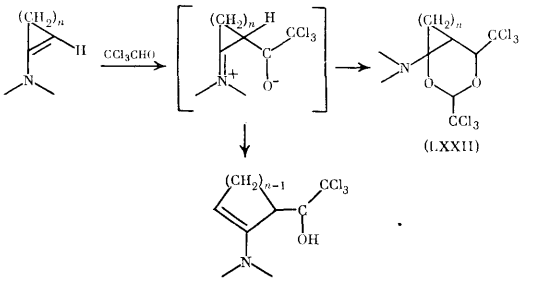


The influence of ring size on the alkylation reaction also follows from an examination of the reactions of β-nitrostyrene with cyclohexynylenamines[121] and cyclopentynylenamines[122]:

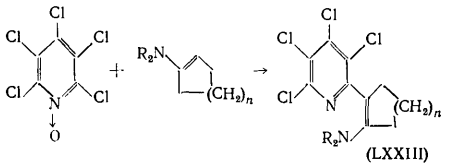


It is noteworthy that such differences are observed also in acylation reactions—in the interaction with methanesulphonyl chloride[121,122].

It has been shown recently that cyclic enamines readily enter into the Mannich reaction in the β-position[123]. The reaction of enamines with chloral also proceeds extremely smoothly[124] and, when the interaction involves two molecules of chloral, bicyclic compounds of type (LXXII) are formed:

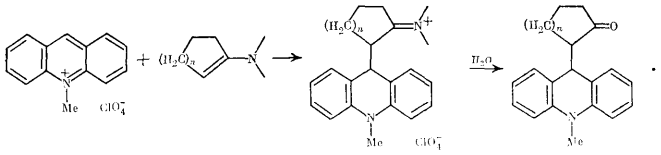


In the presence of a sufficiently mobile halogen atom, aromatic halogeno-compounds can react with enamines. Thus polyhalogenopyridines or their *N*-oxides react with enamines[125] to form β-pyridyl derivatives (LXXIII):

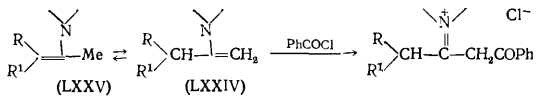


(LXXIII)

Another pathway leading to the β-arylation of enamines has been demonstrated by Chupakhin and co-workers[126,127]— heteroaromatic systems with a marked π-electron deficit were introduced into the reaction. For example:

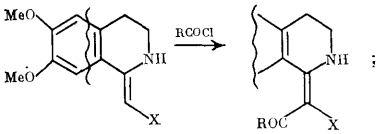


Like alkylation, the enamine acylation reaction can proceed via the nitrogen and/or β-carbon atoms. It has been established[128,129] that, when an isomeric mixture of the tertiary enamines (LXXIV) and (LXXV) is acylated, only the less substituted isomer (LXXIV) reacts:



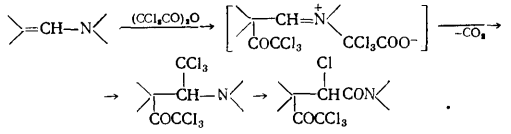
(LXXV) (LXXIV)

Secondary enamines of the isoquinoline series (LXXVI) are *C*-acylated on interaction with acid chlorides[130]:

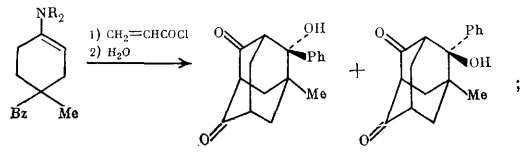


(LXXVI), X = CN, $CONH_2$.

The β-*C*-acylation of enamines by trichloroacetic anhydride is a convenient method of synthesis of amines with α-trichloromethyl and β-trichloroacetyl groups[131]. The subsequent hydrolysis of the compounds obtained is also unusual and leads to α-chloroamides[131]:

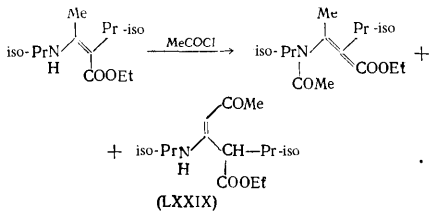


A new interesting method of synthesis of the adamantanediones (LXXVII) and (LXXVIII) is based on the acylation of enamines by unsaturated acid chlorides[132]:



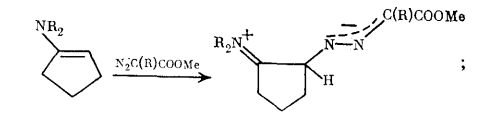
Bz = COPh . (LXXVII) (LXXVIII)

When β-aminocrotonic ester is acylated by acid halides, two (*Z* and *E*) *N*-acylated and *C*-acylated isomers are formed in each case[133]. The reaction of aminocrotonic ester with trifluoroacetic anhydride leads analogously to a mixture of *N*- and *C*-acylenamines[134]. However, if α-alkyl-β-aminocrotonic ester is introduced into the reaction with $(CF_3CO)_2O$, the acylation process proceeds selectively via the amino-group[134]. Similarly, the *N*-alkyl-β-aminocrotonic ester is acylated by acetyl chloride only at the carbon atom and its α-alkyl derivative only at the nitrogen atom[135]. However, in one instance it has been possible to isolate also the *C*-acylation product (LXXIX)[136]:

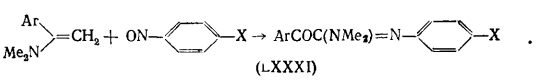


(LXXIX)

It is also noteworthy that β-amino-β-methylvinyl methyl ketone and its *N*-aryl derivative are acylated exclusively at the nitrogen atom[137,138]. In conclusion of this section, we shall mention the reaction of enamines via the β-carbon atom with arenesulphonyl isocyanates (the corresponding *N*-arenesulphonylcarbamido-derivative is formed)[139], the interaction of certain enamines with diazoacetic ester[140] which resulted in the isolation of zwitter-ion of type (LXXX), and the unusual reaction of α-arylenamines with *p*-substituted nitrobenzenes[141], which proceeds with formation of amidines (LXXXI):



(LXXX)



(LXXXI)

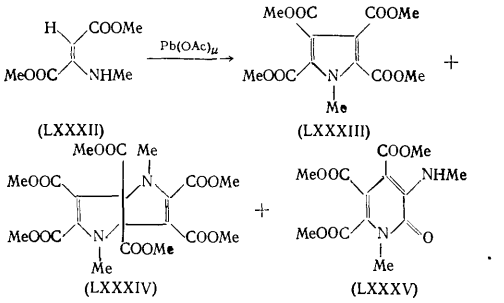
VI. ENAMINES IN THE SYNTHESIS OF HETEROCYCLIC COMPOUNDS

The most promising aspect of the development of the chemistry of enamines at the present time is their employment for the synthesis of various heterocycles. The greatest number of publications concerning the properties and reactions of enamines have been devoted to the problem of such synthesis and this field of study of the class of compounds under consideration is developing most vigorously. As a consequence of this, the syntheses of heterocyclic compounds on the basis of enamines can be usefully surveyed in a single Section of the review, although many of the reactions examined below could naturally be classified also as reactions with nucleophiles or electrophiles, oxidation reactions, reduction reactions, etc. As already mentioned above, many of the heterocyclisation reactions of enamines, which have already been described in recently published reviews[2,5,6], will not be considered in this Section.

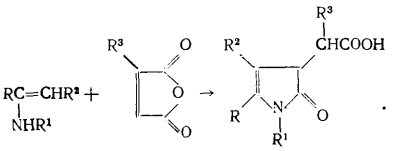
1. Synthesis of Five-Membered Heterocycles

Perhaps the greatest number of publications concerning the synthesis of five-membered heterocycles have been devoted to the preparation of various derivatives of pyrrole.

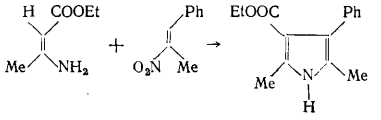
When β-methoxycarbonyl-β-methylaminoacrylic ester (LXXXII) is oxidised with lead tetra-acetate[142], a mixture of 2,3,4,5-tetramethoxycarbonyl-1-methylpyrrole (LXXXIII), pyrrolopyrrole derivatives (LXXXIV), and 2-pyridone (LXXXV) is formed:



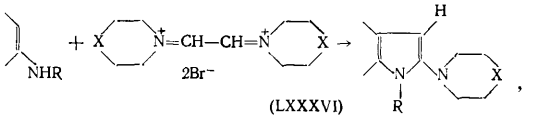
The condensation of secondary enamines with maleic anhydride derivatives leads to 2-pyrrolinone derivatives[143,144]:



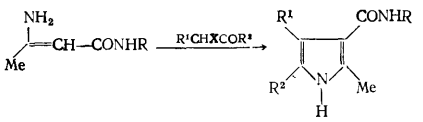
An interesting reaction of primary and secondary enamines with nitroalkenes, which results in the formation of substituted pyrroles, has been described recently[145]:



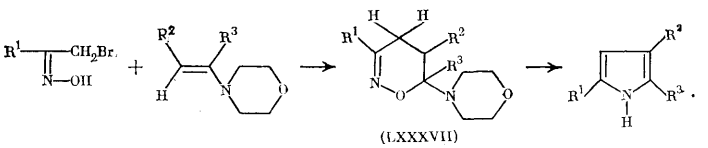
If cyclic enamines or enaminoketones are introduced into this reaction, the products are indole derivatives[145]. Substituted pyrroles have also been obtained by the reaction of enamines with di-immonium dibromide (LXXXVI)[146], i.e.



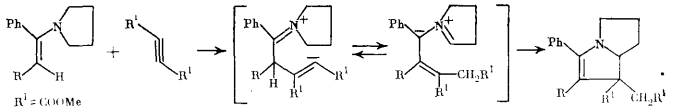
and of enaminoamides with carbonyl compounds[147]:



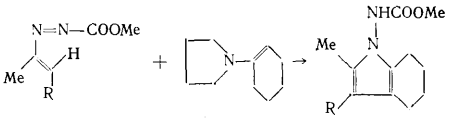
The reaction of enamines with α-bromoximes followed by the decomposition of the intermediate oxazine derivative (LXXXVII) by iron carbonyls also leads to pyrroles[148]:



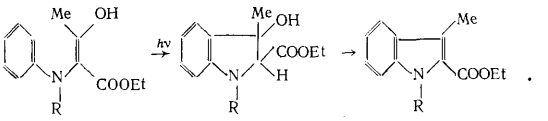
The acetylenedicarboxylic ester attacks β-monosubstituted enamines at the β-carbon atom with subsequent cyclisation to pyrrolizidine derivatives[149]:



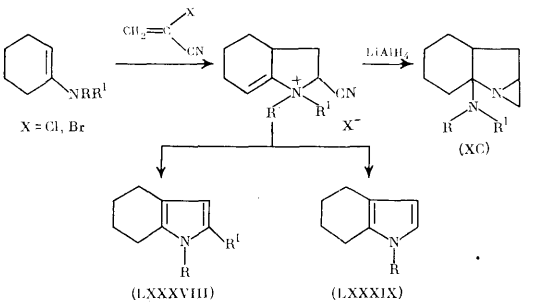
In many instances the employment of enamines ensures a simple and convenient approach to indole derivatives. Thus the condensation of enamines with aza-alkenes leads to hydrogenated indoles[150]:



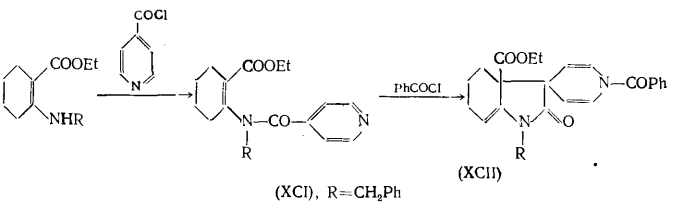
Indoles have also been obtained by the photochemical cyclisation of *N*-arylenamines[151]:



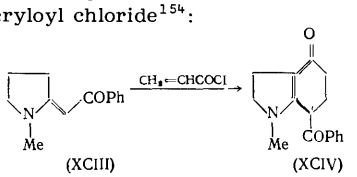
The interaction of enamines with α-halogenoacrylonitriles leads to hydrogenated 2-cyanoindolinium derivatives, which, on treatment with potassium t-butoxide, undergo the Stevens rearrangement and Hofmann elimination with formation of 4,5,6,7-tetrahydroindoles (LXXXVIII) and (LXXXIX), while on reduction with lithium tetrahydroaluminate they are converted into tricyclic hydrogenated indoles of type (XC)[152]:



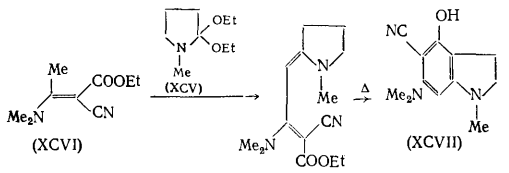
The reaction of the cyclic enamine (XCI) with isonicotinoyl chloride leads to the formation of an *N*-acyl derivative, which cyclises to the spiro-compounds (XCII) on treatment with benzoyl chloride[153]:



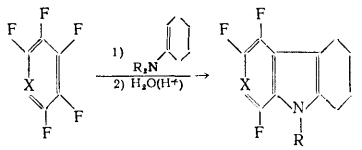
Another method of synthesis of indole derivatives is based on the use of cyclic enamines incorporating in their structure the pyrrolidin-2-ylidene ring[154,155], the functional groups of the side chain of which make possible the growth of an additional benzene ring. Thus hexahydro-4-indolone (XCIV) has been synthesised by the reaction of the enaminoketone (XCIII) with acryloyl chloride[154]:



The reaction of *N*-methylpyrrolidinone acetal (XCV) with the enaminoester (XCVI) followed by thermal cyclisation led to the synthesis of the indoline (XCVII)[155]:

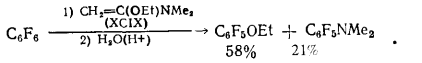


The corresponding benzene, quinoline, and benzazepine derivatives were synthesised in the same investigations[154,155] in accordance with analogous schemes. A number of carbazole derivatives have been obtained by the reaction of hexafluorobenzene with enamines derived from cyclohexanone[156,157]. Pentafluoropyridine reacts analogously[157]:

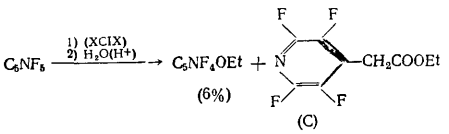


(XCVIII), X=C—F or N

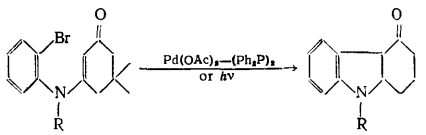
It is of interest that the reaction of compound (XCVIII, X = C—F) with keten *O,N*-acetals (XCIX) leads only to *O*- and *N*-arylation products[157]:



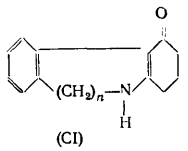
On the other hand, compound (XCVIII, X = N) is capable of β-*C*-arylation of compound (XCIX) with formation of the pyridylacetic ester (C)[157]:



N-Arylenaminoketones having a bromine atom in the *o*-position in the benzene ring cyclise to carbazoles in the presence of a palladium catalyst[158] or on ultraviolet irradiation[159]:

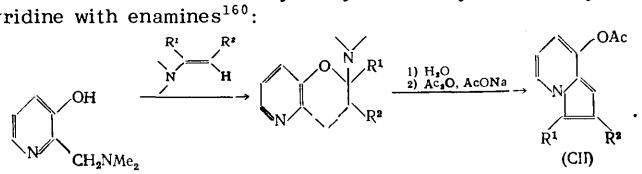


Derivatives of phenanthridine, benzazepine, and benzazocine (CI) have been obtained analogously on irradiation of the corresponding enaminoketones[159]:



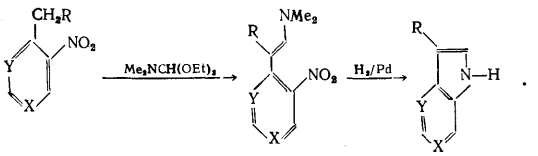
(CI)

An interesting synthesis of pyrrolo[1,2-*a*]pyridine (CII) is based on the reaction of 3-hydroxy-2-dimethylaminomethylpyridine with enamines[160]:



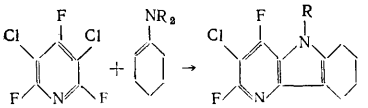
(CII)

Pyrrolo[1,2-*c*]- and pyrrolo[2,1-*b*]-pyridines (CIII) and (CIV) have been synthesised by the reduction of the corresponding nitroenamines (CV) and (CVI)[161–163]:

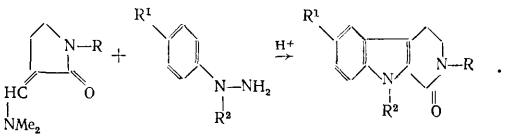


(CV), X = N, Y = CH
(CVI), X = CH, Y = N

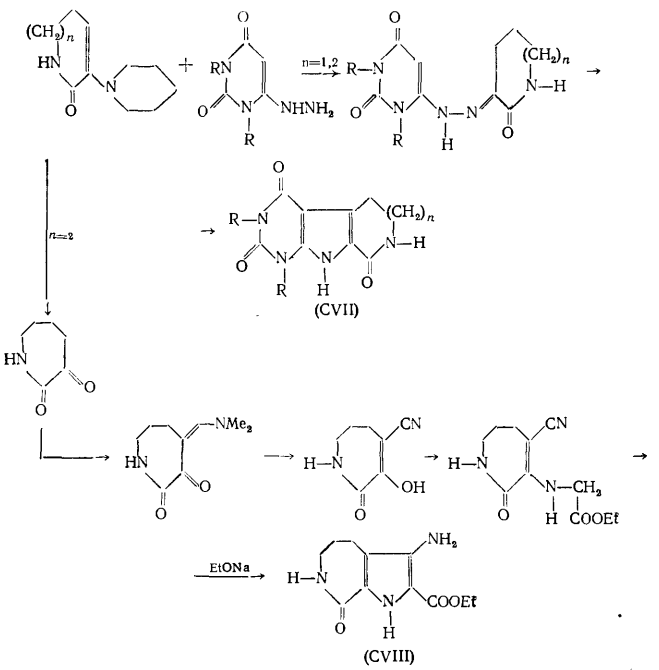
The arylation of enamines by polyhalogenopyridines[125] leads to carbolines:



Another pathway leading to carbolines has been found recently[164] in the study of the reaction of enamines derived from 3-formylpyrrolidinones with arylhydrazines:



Finally we may mention the syntheses of diazacarbolines (CVII)[165] and pyrrolo[2,3-*c*]azepines (CVIII)[166], based on the use of enamines derived from α-oxolactams:

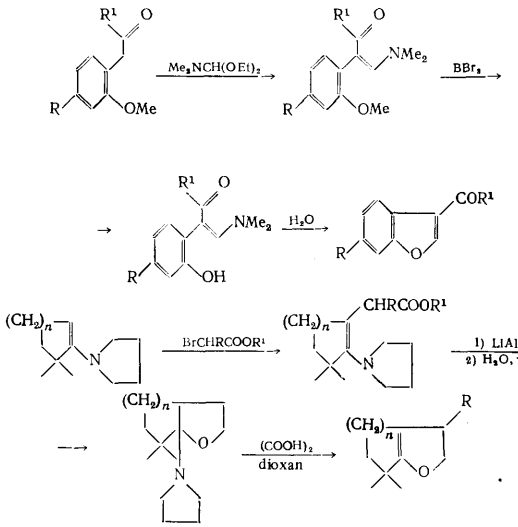


(CVII)

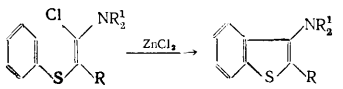
(CVIII)

Comparatively few studies devoted to the synthesis of furan and thiophen derivatives from enamines have been published recently. Furans have been obtained by the cyclisation of the enamine and phenolic groups in the *ortho*-positions relative to one another[167] and by the reaction of cyclic enamines with bromoacetic ester followed by the reduction of the

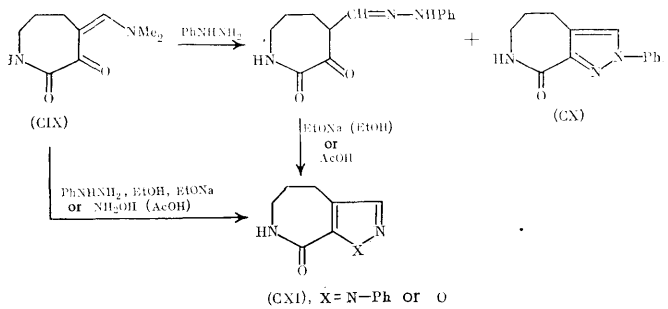
resulting β-*C*-substitution product with lithium tetrahydroaluminate[168]:



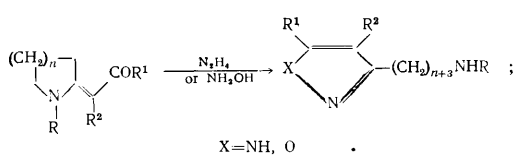
The synthesis of benzothiophens is based on the Friedel–Crafts reaction[169]:



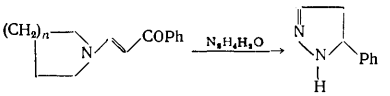
A number of studies have been devoted to the synthesis of azoles, in the first place pyrazoles. Pyrazoles are most often obtained by the reaction of enaminoketones with hydrazine derivatives[84,170-173]. The reaction of enaminoketolactam (CIX) with phenylhydrazine makes it possible to obtain the isomeric pyrazoles (CX) and (CXI) in which X = NPh[84]:



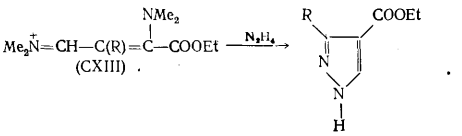
On treatment wth hydroxylamine, compound (CIX) is readily converted into a derivative of isoxazolo[5,4-*c*]azepine (CXI, X = 0).[84] The synthesis of pyrazole (and isoxazole) derivatives by the reaction of cyclic enaminoketones with hydrazine hydrate or hydroxylamine is of interest[173]:



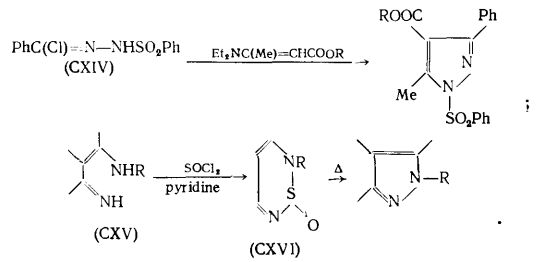
We may also point out that acid catalysis has proved extremely effective in the reactions enaminoketones (CXII) with hydrazine hydrate[171]:



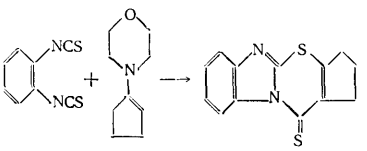
In addition it has been established that the rate of this reaction depends on the ring size and is a maximum for the six-membered cyclic enamine (CXII, $n = 2$) and a minimum for the seven-membered enamine (CXII, $n = 3$)[171]. The interaction of hydrazine with the enaminoimmonium salt (CXIII) is closely related to the above syntheses[174]:



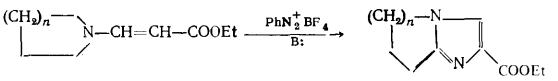
Pyrazoles have also been obtained by the condensation of enamines with diazo-compounds[175] and *N*-(benzenesulphonyl)-benzohydrazonoyl chloride (CXIV)[176] and by the reaction of enaminoimines (CXV) with thionyl chloride and subsequent thermal decomposition of the intermediate 1,2,6-thiadiazine *S*-oxide (CXVI)[177]:



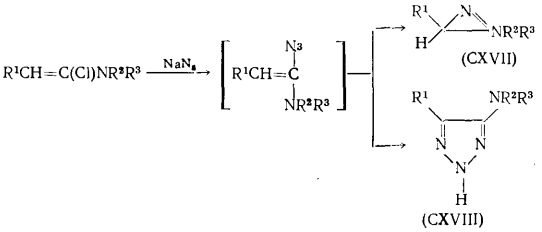
The reactions of cyclic enamines with *o*-phenylene di-isothiocyanate lead to the closure of the imidazole and thiazine rings[178]:



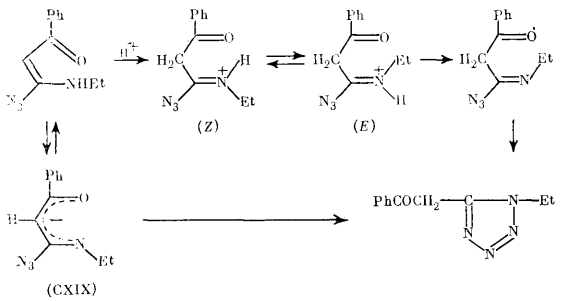
Imidazole derivatives can also be obtained from enaminoesters and arenediazonium salts in the presence of bases[179]:



The interaction of α-chloroenamines with sodium azide[180] leads to various products depending on the substituent at the enamine nitrogen: the azirines (CXVII) are formed from *N*-arylenamines, while the more basic *N*-alkylene-enamines give rise to the triazoles (CXVIII):



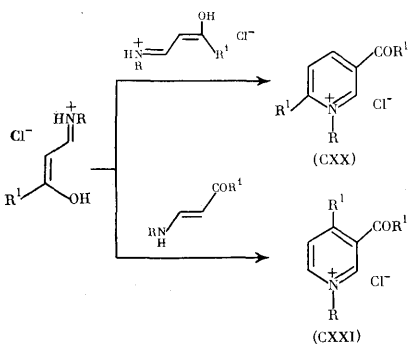
α-Azidoenamines containing the benzoyl group in the β-position (azidoenaminoketones) readily cyclise to tetrazoles[181] and in an alkaline medium the rate-limiting stage of the process is the formation of the anion (CXIX), while in an acid medium the rate-limiting stage is *Z*–*E* isomerisation:



(CXIX)

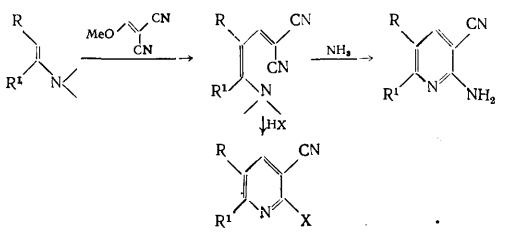
2. Synthesis of Six-Membered Heterocycles

Most of the studies concerning the synthesis of six-membered heterocycles from enamines have been devoted to the synthesis of various pyridine systems and it has been possible to synthesise both monocyclic pyridines and pyridines condensed with various carbocyclic and heterocyclic compounds. Substituted pyridinium salts are formed extremely readily when enaminoketones are treated with acids[182]. However, in this case there is a possibility of both the condensation of two molecules of the *O*-protonated forms and of the interaction of the *O*-protonated form with a neutral molecule. Accordingly, the isomeric pyridinium salts (CXX) and (CXXI) are produced:

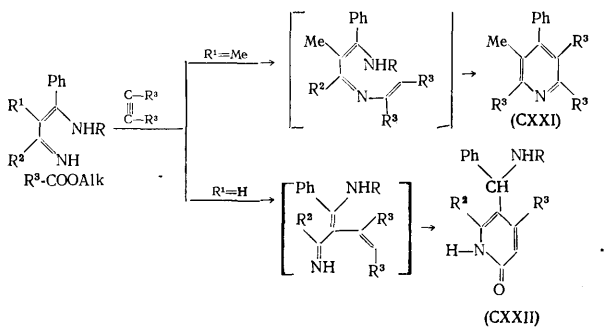


(CXXI)

The interaction of enamines with methoxymethylenemalononitrile followed by treatment with ammonia or acids leads to 3-cyanopyridines[183]:

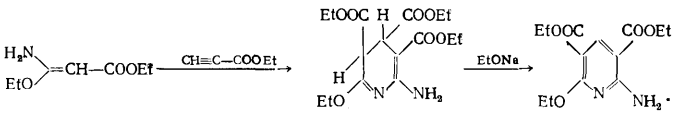


Acetylenedicarboxylic ester can react with enaminoimines[184] in two ways—alkylation of the enamine nitrogen atom results in the formation of derivatives of esters of nicotinic acids (CXXI), while alkylation at the β-carbon atom leads to derivatives of 2-pyridone (CXXII):

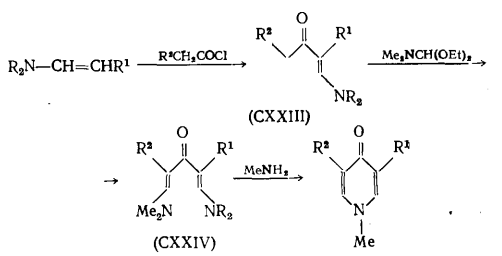


(CXXII)

The interaction of propiolic ester with α-alkoxyenaminoesters leads to derivatives of 2-aminopyridine[185]:

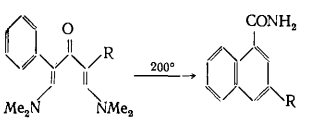


The reaction of two molecules of β-aminocrotonic ester with formaldehyde leads to the formation of 3,5-diethoxycarbonyl-2,6-dimethyl-1,4-dihydropyridine[186]. A convenient synthesis of 4-pyridone derivatives has been developed[187,188] on the basis of the ability of enamines to undergo β-acylation and transamination with primary amines:

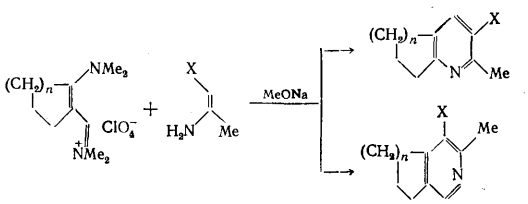


(CXXIV)

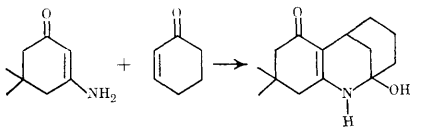
It is of interest that enamines of types (CXXIII) and (CXXIV) are capable of being converted into naphthalene, biphenyl, or diphenyl ether derivatives on heating[189], for example:



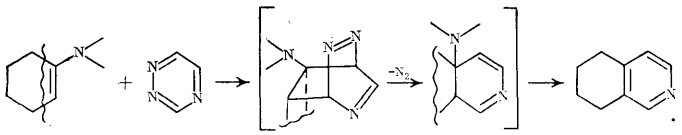
Hydrogenated quinoline derivatives have been synthesised in various ways—by the [4 × 2] cycloaddition of enamines to benzylideneanilines[190], by the reaction of enamines with acrylamide[191], and by the reaction of imines in the form of enamine tautomers with acrylic acid derivatives and propiolactone[192]. The reactions of enamines with enaminoammonium salts proceed via two pathways with formation of isomeric condensed pyridines[193]:



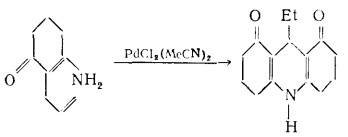
The first stage of the reaction of the enamine derived from dimedone with cyclohexene is *C*-alkylation of the enamine[194]:



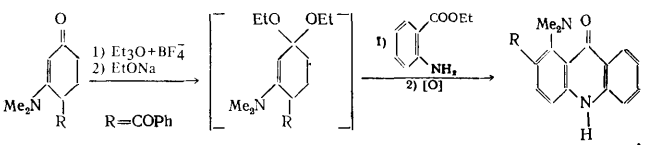
The Diels–Alder reaction, in which enamines behave as dienophiles, is also extremely interesting[195]:



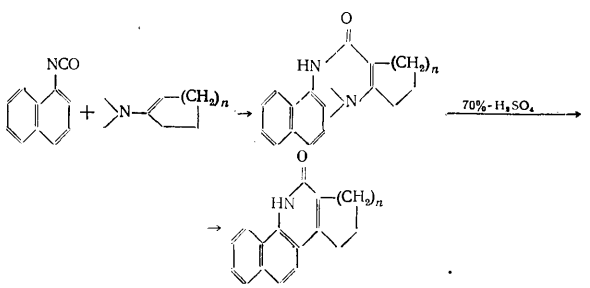
New syntheses of acridines have been developed as a result of the study of the reactions of primary enaminoketones having an unsaturated group in the β-position with the complex $PdCl_2(MeCN)_2$,[196] i.e.



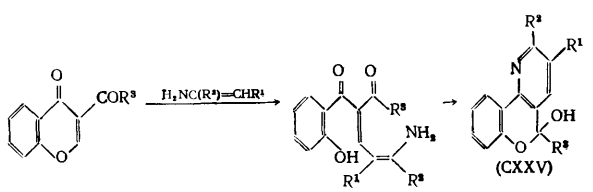
and of the reaction of tertiary enaminoketones with an alkylating agent and then anthranilic ester in accordance with the scheme[197]:



Complex tetracyclic systems containing the pyridone ring have been obtained in the reactions of cyclic enamines with α-naphthyl isocyanates[198,199]:

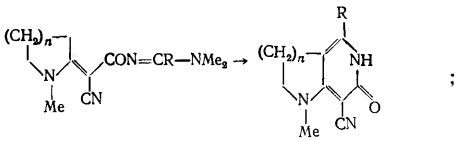


It has been possible to use enamines in a number of syntheses of pyridines condensed with oxygen-containing heterocycles–benzopyranopyridines (CXXV)[200], as well as derivatives of pyrano[4,3-c]pyridines[201], pyrano[2,3-*b*]pyridine[202], and pyrido[4,3-*b*]benzofuran[203]:

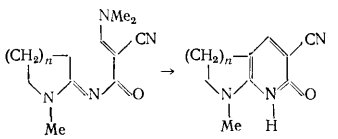


(CXXV)

A number of studies have been devoted to the synthesis of condensed pyridines from enaminoamides[204–208]. The synthesis is based on the preparation and intramolecular cyclisation of enaminoacylamidines of the type (CXXVI, R = H) and (CXXVII)[204,207]. Condensed 2-pyridones can also be obtained from enaminoacylguanidines (CXXVI, R = Me_2N)[209]:

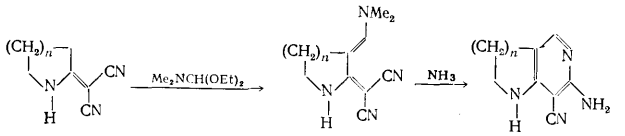


(CXXVI), n=1–3

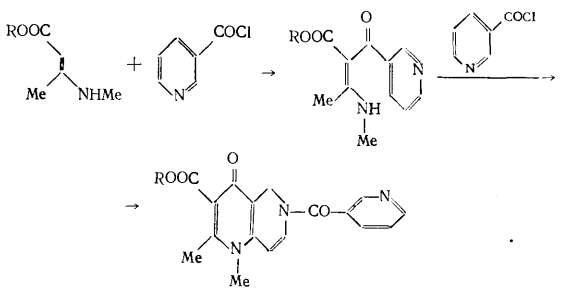


(CXXVII), n = 1–3

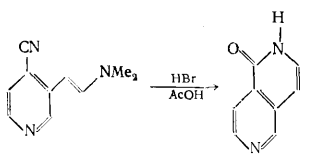
The study of the kinetics of these reactions showed that the cyclisation of compounds (CXXVI) is much faster than that of compounds (CXXVII)[205]. It has been established recently that enaminodinitriles are also convenient compounds for the synthesis of condensed pyridines[210]:



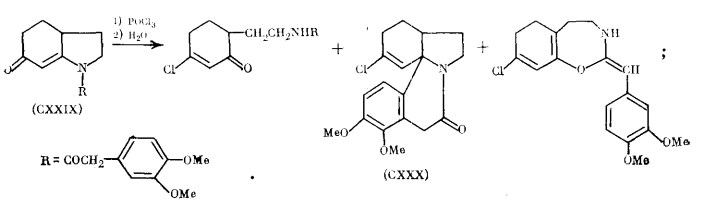
β-*C*-acylation of secondary amines by nicotinoyl chloride with subsequent cyclisation by means of the same reagent leads to 1,5-naphthyridines[153]:



2,6-Naphthyridines have been obtained by the cyclisation of 4-cyano-3-(β-dimethylaminovinyl)pyridines[211]:

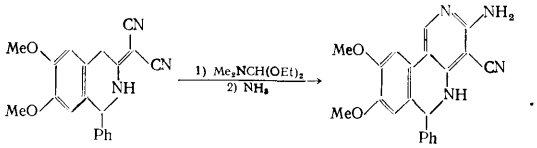


The reactions of certain enaminoketones with phosphoryl chloride and phosphorus pentachloride were discussed above[105]. When this reaction is carried out in acetonitrile, several compounds, including benzoxazepine and indoloquinolone (CXXX), are formed from the enaminoketone (CXXIX)[105]:

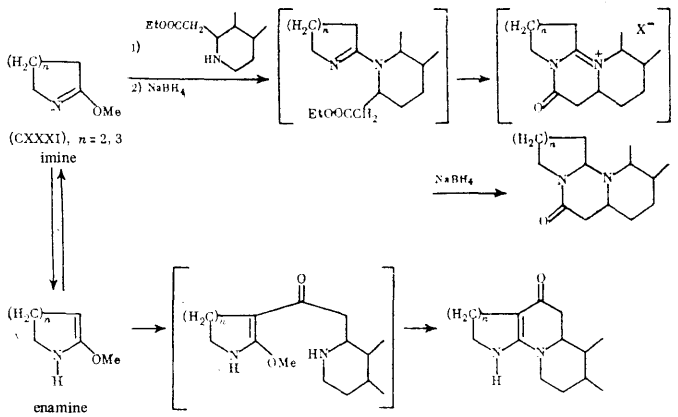


(CXXIX) (CXXX)

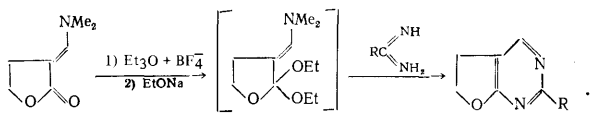
Pyrido[2,1-*a*]isoquinolines have been obtained by the reactions of enamines with 3,4-dihydroisoquinolines[212], while derivatives of the isomeric pyrido[4,3-*c*]isoquinoline system have been synthesised from enamines of the isoquinoline series[212] in accordance with a scheme analogous to that for the synthesis of condensed 2-aminopyridines:



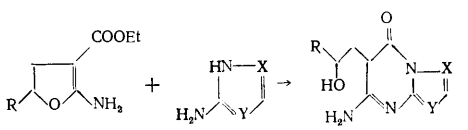
It is of extremely great interest to employ for synthetic purposes[26] the phenomenon of the imine–enamine tautomerism discovered previously[213] in the series of lactim esters. It has been shown[26] that *O*-methylvalerolactim and *O*-methylcaprolactim (CXXXI) react with derivatives of 2-ethoxycarbonylmethylpiperidine as both imines and enamines, giving rise to a mixture of condensed pyridines and pyrimidines:



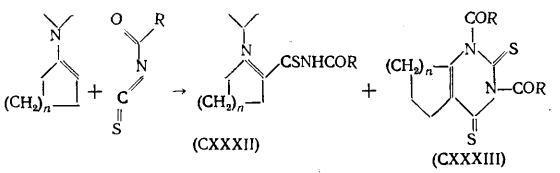
Enaminocarbonyl compounds react fairly readily with guanidine and amidines to form pyrimidine derivatives[197,214]. In a number of instances the carbonyl group must be activated, usually by alkylation[197,215], for example,



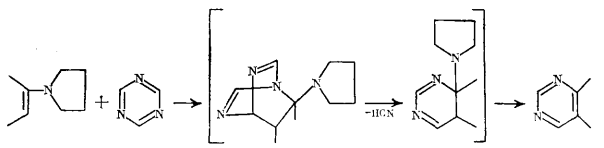
Heterocyclic enaminoesters react with aminoazoles to form azolopyrimidines[216,217]:



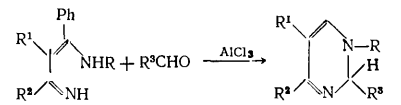
The reactions of enamines with carbonyl isothiocyanates[218] are accompanied by the formation of [1:1] adducts (CXXXII) and [1:2] adducts (CXXXIII):



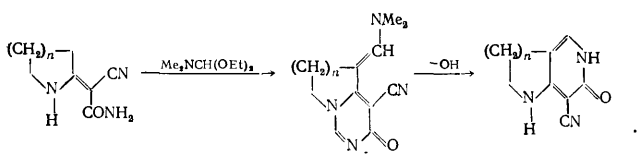
The cycloaddition of enamines to *sym*-triazine leads to pyrimidines[219]:



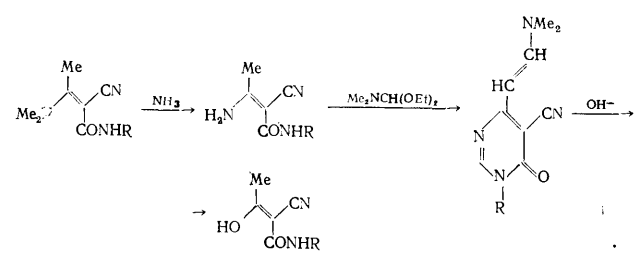
Pyrimidines are also formed when enaminoimines react with aldehydes under the conditions of the Friedel–Crafts reaction[220]:



The condensation of dimethylformamide and dimethylacetamide diethyl acetals with enaminoamides leads smoothly to derivatives of 5-cyanopyrimidine[130,206,210,221–224]. It is significant that the pyrimidines synthesised in this way are readily cleaved in an alkaline medium with subsequent recyclisation to pyridine derivatives. This method of synthesis of pyridine derivatives condensed with a saturated azaheterocycle is in fact preparatively most convenient:

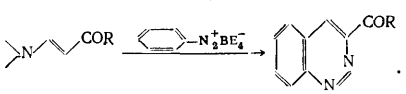


The kinetics of the cleavage of the pyrimidine ring have been investigated[210]. It is of interest that a change in the location of the substituent in the pyrimidine ring lowers the rate of its cleavage and recyclisation does not then occur[224]:



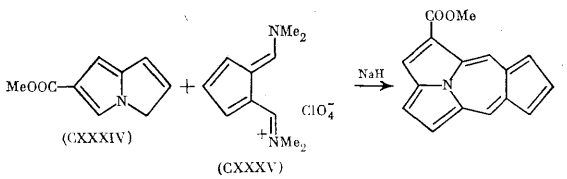
R=PhCH$_2$

A number of studies have been devoted to the closure of six-membered rings other than the pyridine and pyrimidine rings. Thus the interaction of enamines with 1-dialkylaminomethyl-2-hydroxynaphthalenes leads to condensed pyrans[225]. Condensed pyrans are also formed on reduction of 3-(β-ethoxycarbonyl)enamines by lithium tetrahydroaluminate[226]. The reactions of enaminoketones with ketones in the presence of lithiotetramethylpiperidine followed by cyclisation lead to 2,3-dihydro-4-pyrones[227]. Derivates of 2-pyrone have been obtained by the reaction of *N*-carbamidoenaminoketones with cyanoacetic ester and related compounds[228], while 2-morpholino-3-phenyl-3-isoflavene has been obtained by the reaction of 2-hydroxybenzaldehyde with morpholine enamine derived from phenylacetaldehyde[229]. The synthesis of pyridazines, based on the reaction of enaminocarbonyl compounds with diazonium salts[230], and the synthesis of condensed oxadiazines formed when enamines react with diacyldi-imides[231] or with arylacyldi-imides[232] have been described recently:



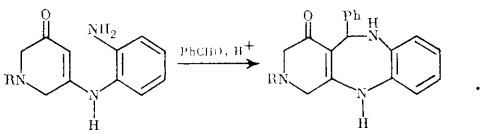
3. The Synthesis of Seven- and Eight-Membered Heterocycles

There have been relatively few studies of the synthesis of heterocycles containing more than six units from enamines. The interaction of *H*-pyrrolizinones (CXXXIV) with the enaminoimmonium salt (CXXXV) in the presence of sodium hydride has been described[233]:

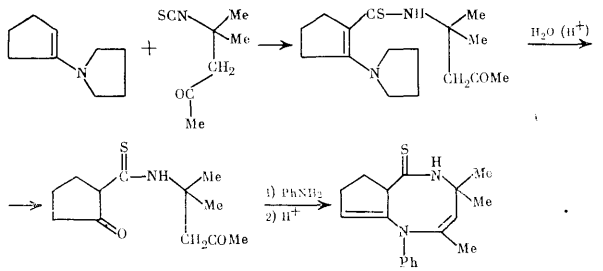


(CXXXIV) (CXXXV)

Condensed diazepines have been synthesised by the reaction of 3-ethoxycarbonylcyclopentanone with 4-nitro-o-phenylenediamine[234] or by the interaction of *N*-arylenamine derived from piperidinedione (CXXXVI) with benzaldehyde[123]:



Finally we shall mention yet another study in which condensed diazocines have been obtained by the reaction of isothiocyanates with the cyclopentanone-based enamine[235] and subsequent treatment with aniline:



Thus the results, presented above, of studies of the properties and the possibility of the employment of enamines in organic synthesis indicate the desirability and likely usefulness of the development of the chemistry of compounds of this class. Further development of studies directed towards the synthesis of various classes of heteromonocyclic, heterobicyclic, and heterotricyclic systems on the basis of enamines is of special interest.

During the preparation of this article for the press, a review was published on the chemistry of enamines[236], which, in contrast to the present review, is concerned mainly with enamines without electron-donating or electron-accepting substituents in the β-position.

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Ordzhonikidze All-Union
Chemico-Pharmaceutical Institute
Moscow

Translated from *Uspekhi Khimii*, 53, 689-714 (1984) U.D.C. 547.66

The Synthesis of Prostaglandins From Cyclopentane Derivatives

V.A.Dombrovskii, D.Yu.Fonskii, V.A.Mironov, and P.M.Kochergin

The advances in the synthesis of prostaglandin derivatives are examined.
The bibliography includes 129 references.

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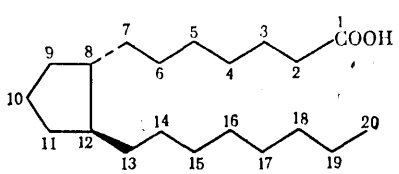
I. INTRODUCTION

Prostaglandins (PG) are biologically active substances with an extremely broad spectrum of action. The influence of PG on the smooth musculature of various organs, their hormone-like and antihormonal activity[1,2], etc. are being investigated at the present time. The therapeutic effect of these compounds is achieved when they are administered in extremely low amounts, of the order of nanograms. This justifies the use of PG as promising medicinal preparations in medicine (cardiology, gastroenterology, midwifery, gynaecology, etc.) and animal husbandry (regulation of the reproductive function of animals). PG and their principal precursors—polyunsaturated aliphatic acids (eicosatetraenoic and eicosatrienoic acids)—are contained in all mammalian tissues but as a rule in extremely small amounts. The highest content of PG is present in the seminal fluids of mammals and man. Thus the overall content of PG in human seminal fluid is on average 213–240 μg ml^{-1} and varies with age and state of health. The seminal fluid of the ram contains approximately 50 μg ml^{-1} of PG. PG has been found also in prostate glands, ovaries, brain tissue, the mucous membranes of the stomach and the intestine, spleen, kidneys, liver, pancreas, and the iris of the eye[3] but at a concentration many times smaller than in the seminal fluid of the ram and man, so that such tissues cannot serve as sources of large amounts of pure PG preparations.

The main natural sources of PG are their close precursors present in the gorgonia *Plexaura homomalla* at an unusually high concentration—2.6 wt.% relative to the dry weight[4].

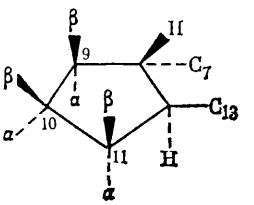
The need for large amounts of PG, which are essential for experimental and clinical studies, combined with the high cost of the preparations (up to 3000 dollars per gram) promoted a vigorous development of methods for the isolation and purification of PG and also stimulated the search for methods of synthesis of PG or their analogues.

PG are derivatives of the hypothetical prostanoic acid (I), the C(8)–C(12) atoms of which are incorporated in the cyclopentane ring (CPR):

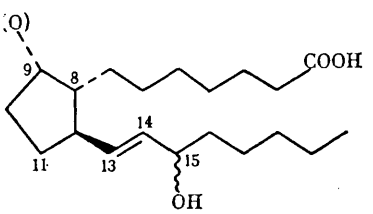


(I)

The CPR substituents are designated by the letter α when they are located on the same side of the plane of the ring as the carbon atom in the 7-position and by the letter β when they are on the other side:

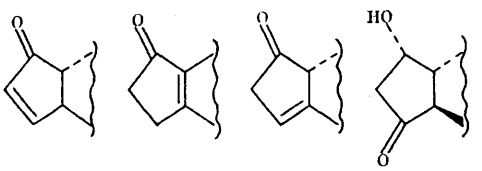


The C(1)–C(7) chain, terminating in a carboxy-group, is designated by convention as the α-chain (or the upper chain) and is located behind the CPR plane. All the PG are characterised by the presence of an oxygen-containing functional group (OH or C=O) at C(9), a hydroxy-group at C(15), and a *trans*-double bond between C(13) and C(14):

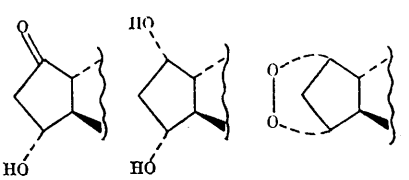


(II)

Depending on the number and type of the oxygen-containing functional groups, the degree of unsaturation of the CPR, and the position of the double bond in the latter, PG are divided into groups designated by the Latin letters, A, B, C, D, E, F, G, and H:



A B C D



E F_α G, H

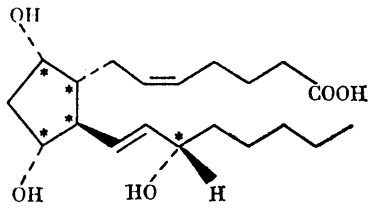
The degree of unsaturation, i.e. the number of double bonds in the PG molecule (in the side chains), is designated by the corresponding numerals: for example PGE_1 has only one C(13)–C(14) *trans*-double bond, PGE_2 has an additional

cis-double bond in the C(5)–C(6) position, and PGE_3 is characterised by the presence of a third *cis*-double bond in the C(17)–C(18) position. Analogous double bonds are also encountered in PG of other groups. As a consequence of the asymmetry of their molecules, PG exist in several isomeric forms. In natural PG the hydroxy-groups in the C(9), C(11), and C(15) positions always have the α-configuration (the PG in group F can exist in two isomeric forms relative to the hydroxy-group at the C(9) atom, namely α and β, which are always indicated after the numeral). Only the isomeric α-forms $PGE_{1,2,3\alpha}$ are encountered in nature. The PG in groups G and F are usually referred to as "basic" or "primary". In a pure form, PG are colourless crystalline powders readily soluble in organic solvents.

When the basic PG molecule is modified chemically by a particular group which is accompanied by a shortening of the alkyl chain, the prefix "nor" is added to the name of the PG; nor implies the shortening of the chain by one methyl group, dinor the shortening by two methyl groups, trinor the shortening by three methyl groups, etc. The number of the missing methyl group is also indicated. When the alkyl chain is lengthened, the prefix "homo" is added to the name of the PG with the simultaneous indication of the number of the new methyl groups (homo- dihomo-, trihomo-, etc.) and the number of the carbon atom to which the methyl group has been attached.

II. THE SYNTHESIS OF PROSTAGLANDINS

After the structure of the PG had been established[5], the synthesis of hormones of this class aroused much interest among synthetic chemists. The total synthesis of natural PG presents considerable difficulties not so much because of the lability of the compounds as due to the complexity of their chemical structure. PG can contain in their molecules up to five asymmetric centres, four of which are in the prostanoid ring and one in the side chain at the C(15) atom, so that the main problem in the total synthesis of PG is the stereospecific construction of these asymmetric centres. Thus the stereocontrolled syntheses of natural PG are in the main multistage processes and the yields of the final products are comparatively low:



($PGF_{2\alpha}$)

Analysis of the literature data makes it possible to divide the methods of synthesis of PG into three main groups:

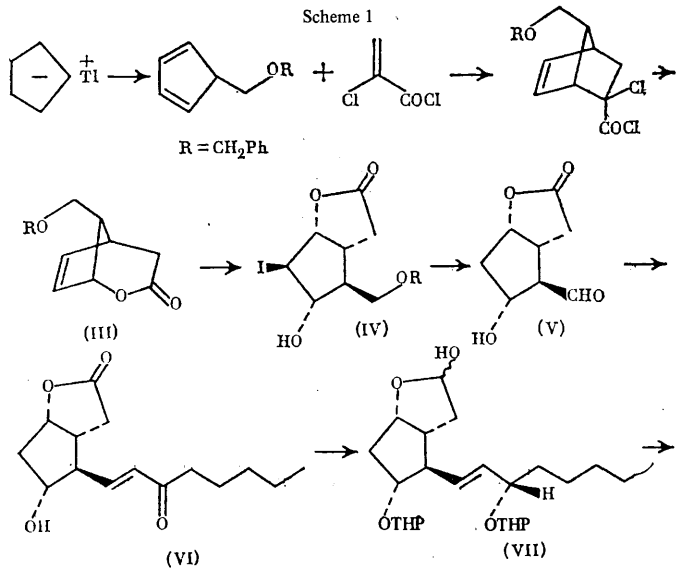
1. The synthesis of acyclic long-chain compounds in which the CPR is closed in one of the last stages.
2. The syntheses of PG from cyclopentane derivatives.
3. The enzymic synthesis from polyenoic acids (biosynthesis).

The growing interest in the second group of methods can be accounted for, on the one hand, by the relative availability of the initial cyclopentane derivatives and, on the other, by the comparative simplicity of the subsequent building up of the PG molecule. However, numerous studies in this field have been scarcely treated systematically and have not been surveyed. Mitra's monograph[6] is devoted to the synthesis of PG or their analogues without referring to the employment of cyclopentanes with functional-group substituents†; the review of Levkoeva and Yakhontov[7] is concerned with the synthesis of heterocyclic analogues of PG. Only a small amount of attention is devoted to PG in Azhgikhin's book[3]. A review dealing with the steric control in the synthesis of PG from bicyclic and tricyclic intermediates was published in 1980.[8] We therefore thought it useful to examine the most important studies on the synthesis of PG from cyclopentane derivatives.

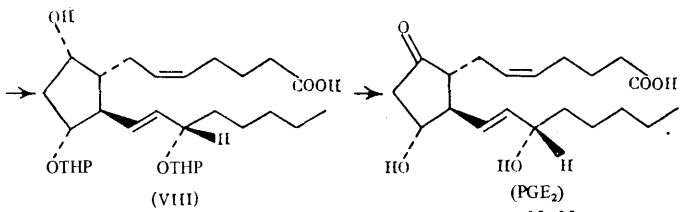
1. Synthesis From Bicyclic Compounds

One of the most significant achievements in the synthesis of PG is the practical application of bicyclic compounds which subsequently make it possible to proceed readily to the total synthesis of PG or their analogues. The key compound in these syntheses is the aldehydolactone (V) which is known in the literature as "Corey's aldehyde". One of the methods of synthesis of this compound[9–12], from cyclopentadienylthallium, is indicated in Scheme 1. The product of the interaction of the thallium derivative with benzyl chloromethyl ether is condensed with the dienophile, namely the chloride of 2-chloroacrylic acid, and the corresponding bicyclic compound is obtained, which is then converted by a series of reactions into 2-oxabicyclo[3.2.1]nonane (III). After the hydrolysis of compound (III) and subsequent treatment with potassium tri-iodide, the iodolactone (IV) is formed. This compound has the necessary configurations of all the nuclear centres. Its acylation, deiodination, and the conversion of the hydroxybenzyl group into an aldehyde group lead to the aldehydolactone (V), which then undergoes the Wittig condensation with the corresponding phosphorane to form compound (VI). The C(15)-keto-group is stereospecifically reduced and, after the conversion of the lactone into the lactol (VII), the α-chain is introduced by the Wittig reaction. Mild hydrolysis of the ester group leads to the intermediate (VIII). After the oxidation of the hydroxy-group at C(9) in compound (VIII) and the removal of the tetrahydropyranyl (THP) protecting group, PGE_2 is isolated. The conversion of compound (VIII) into PGE_1 is achieved by hydrogenating the former over a palladium catalyst.

Scheme 1



† See also J.S.Bindra and R.Bindra, "Prostaglandin Synthesis", Acad.Press, New York–San Francisco–London, 1977.

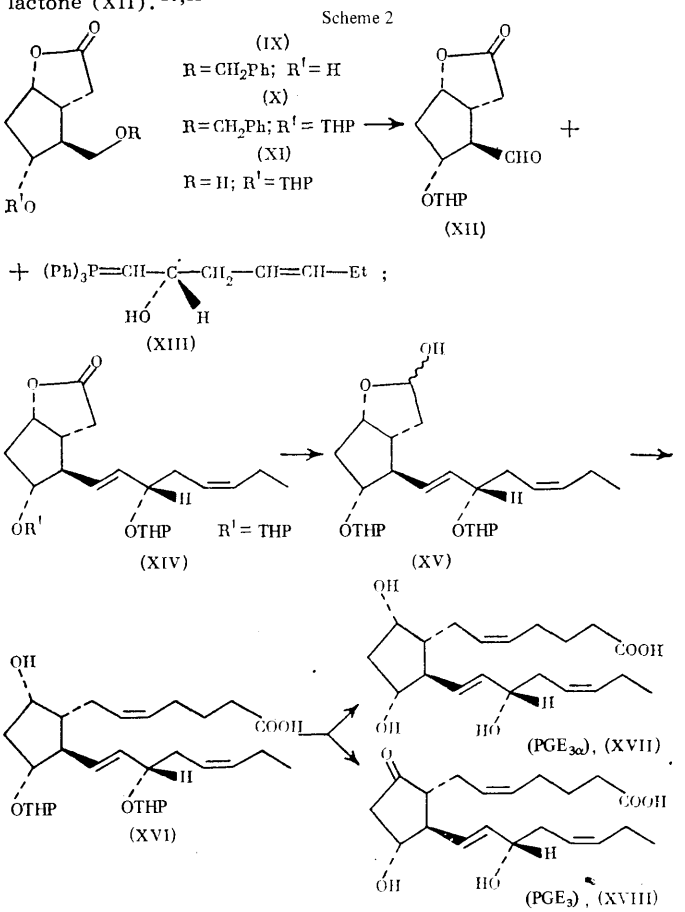


(VIII) (PGE$_2$)

Corey's aldehyde and its various modifications[13–18] have become key compounds in the various syntheses of PG. Thus the optically active PGE$_3$ and PGF$_{3\alpha}$ were synthesised for the first time from the optically active hydroxylactone (IX) (Scheme 2). The lactone (IX) was converted into the aldehyde (XII) after the protection of the hydroxy-group with THP, hydrogenation over Pd/C, and Collins oxidation ($2C_5H_5N.CrO_3$ in CH_2Cl_2) of the resulting alcohol. By condensation with the (*S*)-(+)-phosphonium salt (XIII), the aldehyde (XII) was converted stereospecifically into the unsaturated alcohol (XIV). After conversion into the bis-THP derivative, the allyl alcohol (XIV) was reduced with di-isobutylaluminium hydride (DIBAH) to the lactol (XV). The upper chain in compound (XVI) was built up stereospecifically by the Wittig reaction between the lactol (XV) and 5-triphenylphosphonovaleric acid. The removal of the THP protecting group on acid hydrolysis gives rise to PGF$_{3\alpha}$ (XVII) with $[\alpha]_{D^{26}} = +29.6°$. The oxidation of compound (XVI) with the Jones reagent (chromic acid–acetone) and subsequent removal of the THP protecting group and chromatographic separation lead to PGE$_3$ (XVIII) with $[\alpha]_{D^{24}} = -48.9°$.

PGE$_1$ and PGF$_{1\alpha}$ have been obtained analogously from the lactone (XII).[20,21]

Scheme 2

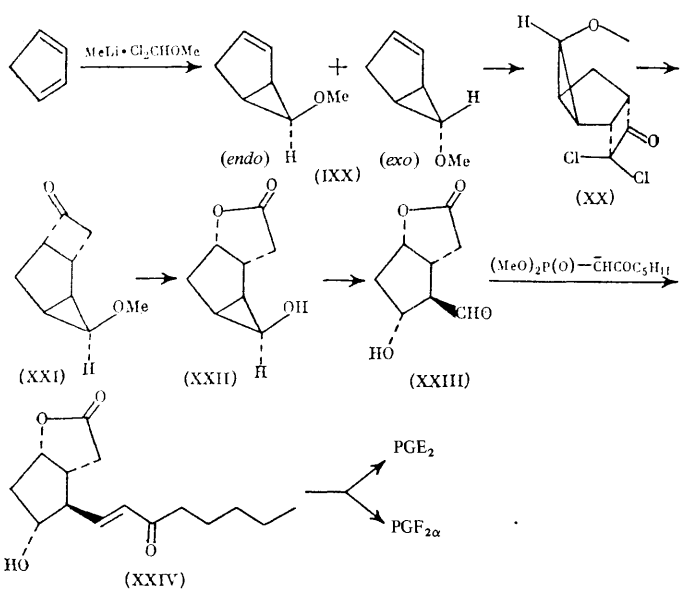


After the successful synthesis of PG using Corey's aldehyde, new methods of synthesis of key compounds from readily available reagents permitting an easy transition to the total synthesis of PG were sought. Thus Corey et al.[22] used 6-methoxybicyclo[3.1.0]hex-2-ene (XIX) as the key compound in the synthesis of PGE$_2$ and PGF$_{2\alpha}$ (*dl*), which were obtained by the condensation of dichloromethyl ethyl ether with cyclopentadiene as a 4:1 mixture of the *endo*- and *exo*-forms (Scheme 3). Refluxing of the 4:1 mixture with dichloroacetyl chloride in an excess of triethylamine leads to the tricyclic ketone (XX) whose dechlorination with zinc dust in glacial acetic acid followed by treatment of compound (XXI) with boron tribromide in CH_2Cl_2 results in the formation of the *endo*-cyclopropanol (XXII). The oxidation of compound (XXII) with a solution of H_2CrO_4 and $Ce(NH_4)_2(NO_3)_6$ in aqueous acetic acid leads to a mixture of three products, one of which is the required hydroxyaldehyde (XXVI). The aldehyde (XXIII) is fairly unstable and for this reason it is immediately condensed with the sodium derivative of 2-oxoheptylphosphonate whereupon a mixture of products is obtained, from which the lactone (XXIV) is isolated chromatographically. Next the lactone (XXIV) is converted into the acetate derivative and then into PGE$_2$ and PGF$_{2\alpha}$ by standard methods.

11-Deoxy-PGE was synthesised in accordance with an analogous scheme by the reaction of 2-(6′-methoxycarbonylhexyl)cyclopent-2-en-1-one with dimethylsulphuranylidene acetate[23,24].

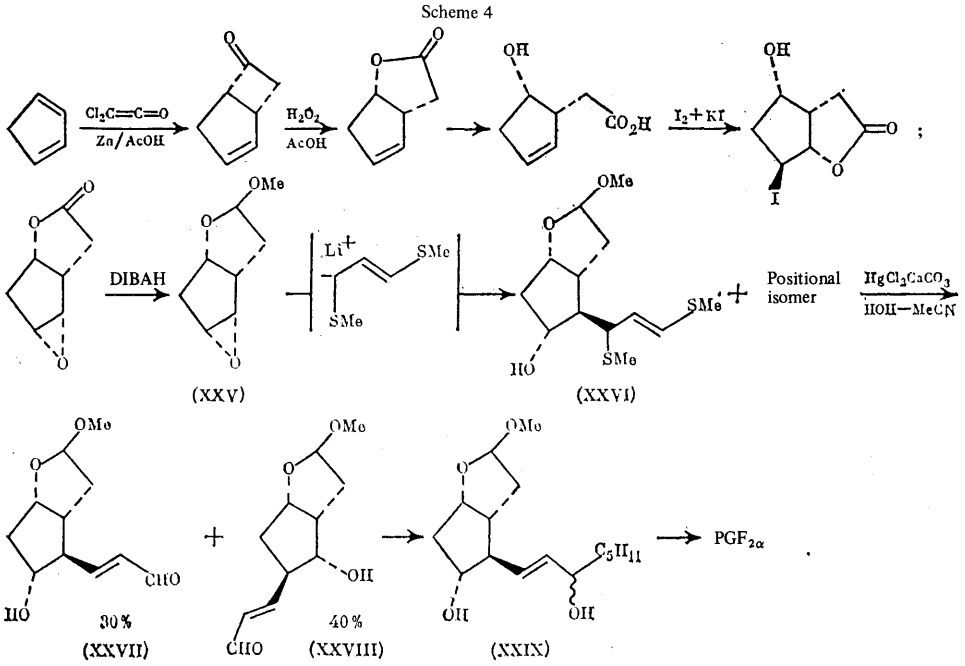
However, the oxidative opening of the cyclopropanol (XXII) ring to give the aldehyde (XXIII) proceeds with a low yield and for this reason Corey and Hayozi[25] developed a new approach to the synthesis of PGF$_{2\alpha}$ via the epoxidation of unsaturated bicyclic derivatives of cyclopentanone with subsequent regioselective opening of the oxide ring by the lithio-derivative of the vinyl sulphide MeS–CH_2–CH=CH–SMe (the β-nucleophilic equivalent of –CH=CH–CHO) which contains the potential C(13)–C(14) *trans*-double bond (Scheme 4).

Scheme 3



Condensation of the epoxyacetal (XXV) with 1,3-di(methylthio)allyl-lithium gives a mixture of the required product (XXVI) and its postional isomer. Hydrolysis of the mixture leads to a mixture of two unsaturated aldehydes, (XXVII) and (XXVIII), which were separated on a preparative scale.

Scheme 4

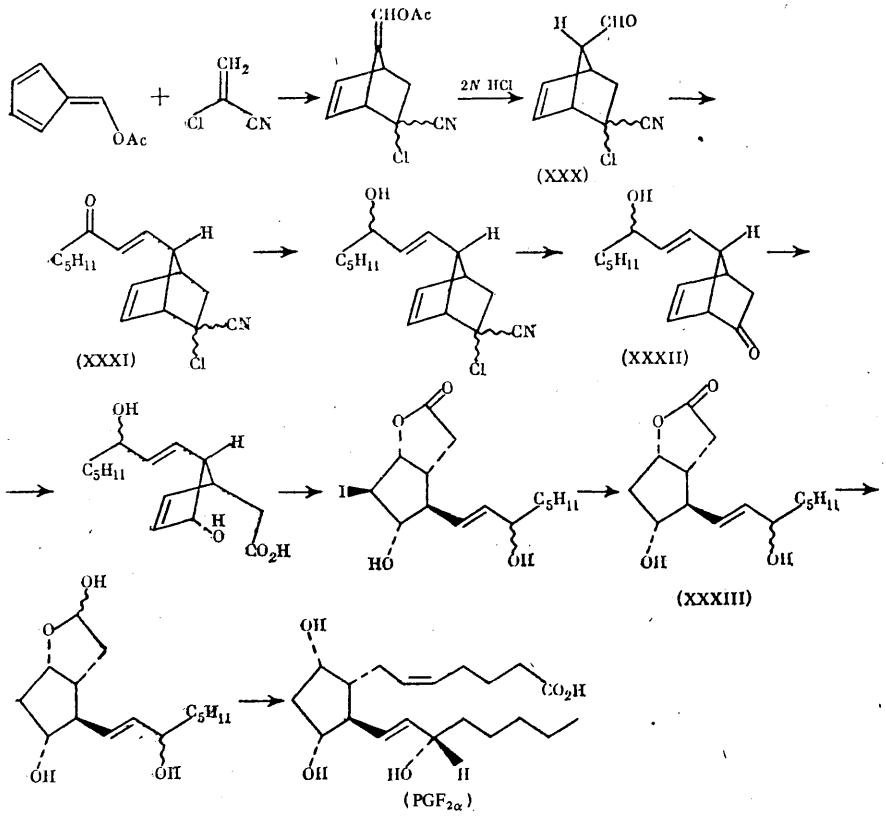


The condensation of the more polar aldehyde (XXVII) with n-butyl-lithium leads to a mixture of approximately equal amounts of the epimeric secondary alcohols. The acid hydrolysis of the more polar compound (XXIX) with subsequent isolation of the lactol and its condensation with the sodium derivative of 5-triphenylphosphonopentanoic acid yields $PGF_{2\alpha}$. The less polar epimer (XXIX) was converted in two stages into *dl*-15-epi-$PGF_{2\alpha}$ in the same way.

In a later study ring opening in the tricyclic epoxide (XXV) in the total synthesis $PGF_{2\alpha}$ was achieved with a higher regioselectivity on treatment with divinyl cuprate[26].

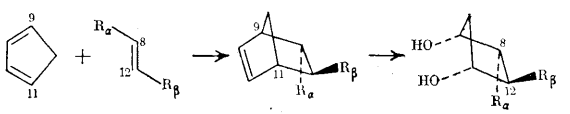
An alternative synthesis of $PGF_{2\alpha}$ is based on the employment of acetoxyfulvene as the starting compound[27-31] in the synthesis of the key compound (XXX) via Scheme 5:

Scheme 5



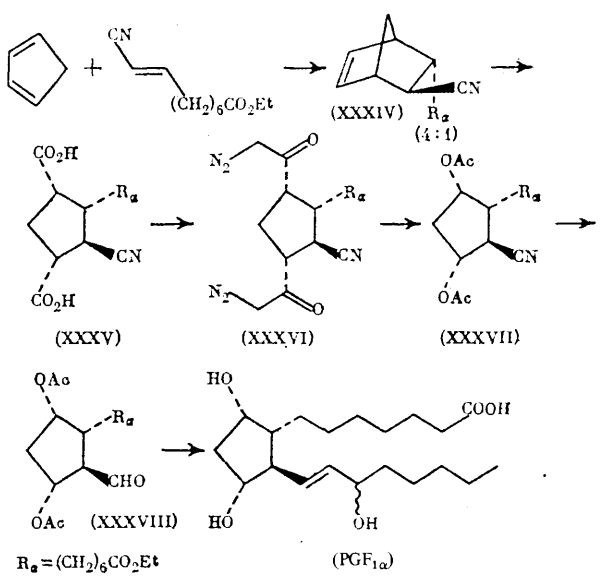
The bicycloheptenal (XXX) reacted with the lithio-derivative of dimethyl 2-oxoheptylphosphonate with formation of the *trans*-enone (XXXI) whose reduction with DIBAH and subsequent alkaline hydrolysis of the chloronitrile group lead to the ketone (XXXII). Baeyer–Villiger oxidation (H_2O_2, KOH) of compound (XXXII) and the iodolactonisation of the hydroxyacid salt formed *in situ* lead to the iododiol whose deiodination with tri-n-butyltin hydride affords the diol (XXXIII). After the reduction of compound (XXXIII) by DIBAH to the *gem*-acetal (XXXIV) and its condensation with the sodium salt of (4-carboxybutyl)triphenylphosphorane, $PGF_{2\alpha}$ was obtained together with the C(15)-epimer. Chromatographic separation of this mixture makes it possible to obtain the racemic $PGF_{2\alpha}$. The conversion into PGE_1 of the A and B series was achieved by standard methods[9].

5,6-Disubstituted bicyclo[2.2.1]hept-2-enes can serve as convenient precursors for the construction of PG. This strategy in the synthesis was first developed and modified by Katsube and co-workers[32–36]. The disubstituted bicyclo[2.2.1]-heptene is obtained by the Diels–Alder reaction between cyclopentadiene and the corresponding substituted *trans*-olefine, the dienophile giving rise to the C(8) and C(12) atoms incorporated in the cyclopentane ring:



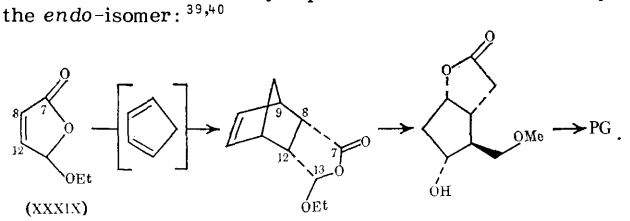
One of the examples of this approach is the synthesis of $PGE_{1\alpha}$ [32] (Scheme 6).

Scheme 6

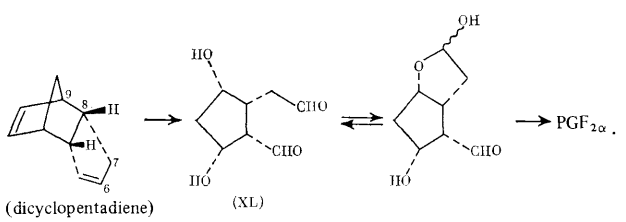


The Diels–Alder reaction between 2-cyano-9-ethoxycarbonyl-*trans*-non-2-ene, obtained by a standard method in four stages from diethyl suberate and cyclopentadiene at 150 °C in an autoclave, leads to a mixture of *exo*-2-cyano-3-(6'-ethoxycarbonylhexyl)bicyclo[2.2.1]hept-5-ene (XXXIV) and the corresponding *endo*-derivatives in proportions of 4:1, which were separated by chromatography on silica gel (SG). The ozonolysis of the *exo*-derivative of compound (XXXIV) and subsequent oxidative decomposition of the ozonide with an aqueous solution of performic acid yielded 3,5-dicarboxy-1α-cyano-2-β-(6'-ethoxycarbonylhexyl)cyclopentane (XXXV). Treatment of the latter with phosgene in a DMF–benzene mixture led to an acid dichloride, which gave rise, after treatment with a solution of diazomethane in ether, to the corresponding bisdiazoketone (XXXVI), which was converted into 3,5-diacetyl-1α-cyano-2β-(6'-ethoxycarbonylhexyl)cyclopentane (XXXVII). The oxidation of compound (XXXVII) with *m*-$ClC_6H_4CO_3H$ in $CHCl_3$ gave rise to 3,5-diacetoxy-2β-(6'-ethoxycarbonylhexyl)-1α-formylcyclopentane (XXXVIII), which was subsequently made to react with $Bu_3P{=}CH{-}CO{-}(CH_2)_4Me$, the condensation product was separated chromatographically, the C=O group at C(15) was reduced with sodium tetrahydroborate, the acetate protecting group was removed by hydrolysis, and $PGF_{1\alpha}$ was obtained.

It is noteworthy that this approach[32–38] to the synthesis of PG suffers from a significant disadvantage, since the reaction between cyclopentadiene and the corresponding substituted *trans*-olefin produces a mixture of the *exo*- and *endo*-adducts whose separation creates additional difficulties. However, the use of compound (XXXIX) (the β-formylacrylic acid pseudoester) as the dienophile in the Diels–Alder reaction with cyclopentadiene leads exclusively to the *endo*-isomer:[39,40]



An interesting 13-stage stereoselective synthesis of $PGF_{2\alpha}$, where the key compound is Turner's intermediate (XL), obtained from the readily available *endo*-dicyclopentadiene by successive oxidation, has been achieved[41,42]:



However, in this case the Diels–Alder reaction with symmetrically substituted dienophiles should not be carried out. The cyclopentene ring in dicyclopentadiene serves as a source of one or two aldehyde groups which are essential for the subsequent construction of the α- and β-chains of PG respectively.

It is also possible to use 3-alkylcyclopentane-1,2,4-triones but only to a limited extent, since in this case the synthesis consists of many stages[43–48]. Thus the synthesis of *dl*-$PGF_{1\alpha}$ has been achieved (Scheme 7). 5-Ethoxycarbonyl-3-(3-methylbut-2-enyl)cyclopentane-1,2,4-trione (XLI) has been obtained by the cyclisation of two molecules of 6-methylhept-5-en-2-one and four molecules of $(COOC_2H_5)_2$. Subsequent treatment with alkali and then acid yields compound (XLII) and conversion into the acetal following treatment with orthoformic ester and subsequent condensation with 1-heptyl-7-methoxymagnesium bromide lead to the dione (XLIII). The latter was reduced initially with Zn/HOAc and then with Li/NH_3 to form a mixture of diols, whose catalytic hydrogenolysis gave rise to the corresponding cyclopentanediols (XLIV). Treatment

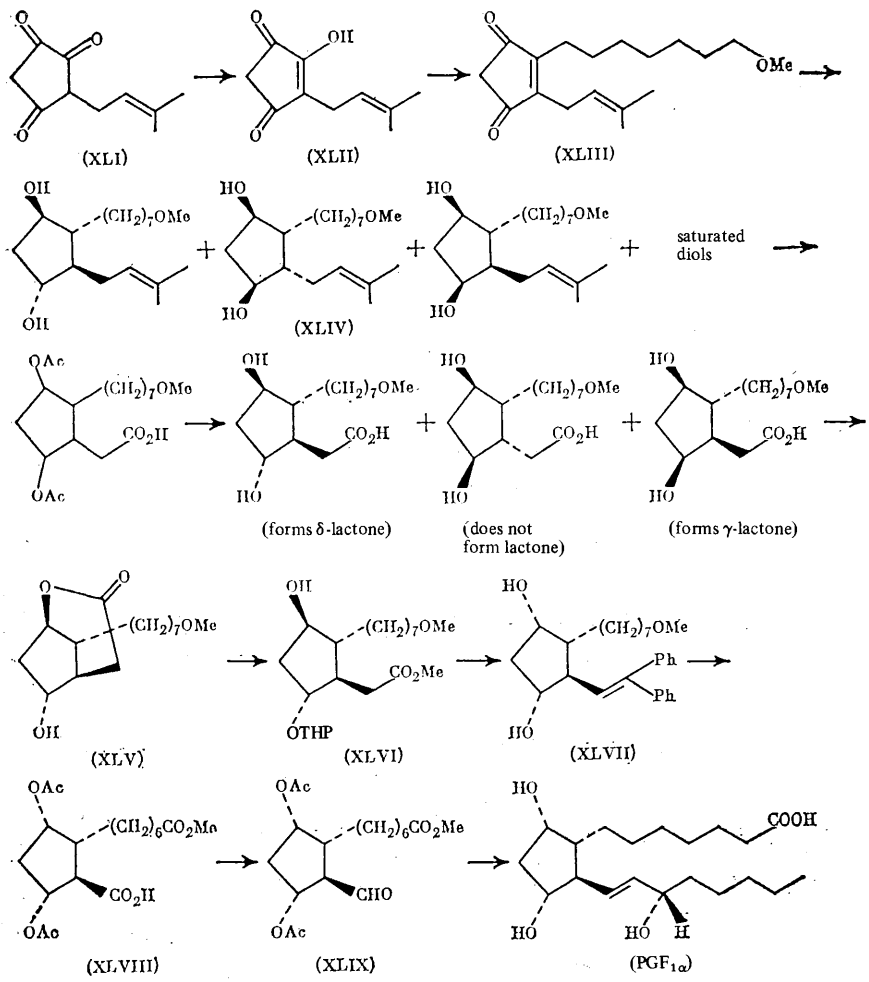
of the diols (XLIV) with acetic anhydride and oxidation with a mixture of $KMnO_4$ and $NaIO_4$ produced the corresponding diacetates of the acids, whose hydrolysis afforded the diols. The latter were converted into the δ-lactone (XLV) on treatment with TsOH. The OH group at C(11) in the δ-lactone (XLV) was protected with THP, after which the product was subjected to alkaline hydrolysis and was treated with an ethereal solution of diazomethane. The OH groups at C(9) in the resulting ester (XLVI) were protected and the latter was condensed in the form of the acetate with phenylmagnesium bromide. The diol (XLVII) was obtained on acidification. After the protection of the hydroxy-groups in compound (XLVII) with acetic anhydride, the methoxy-group was cleaved with boron tribromide to give the hydroxy-group and the subsequent oxidation of this group with the RuO_4–$NaIO_4$ mixture and esterification with diazomethane led to the ester-acid (XLVIII). The reduction of the carboxy-group with diborane and its subsequent Collins oxidation afforded the required aldehyde (XLIX), whose condensation with the corresponding phosphonate, the reduction of the C=O group at C(15) with $Zn(BH_4)_2$, and acid hydrolysis produced $PGF_{1\alpha}$.

2. Synthesis via the Coupled Addition of Organometallic Derivatives

The 1,4-addition of organometallic reagents to 4-alkoxy-2-alkylcyclopent-2-enones, which makes it possible to proceed readily to the total synthesis of PG, has been fairly widely used recently. The addition of divinyl cuprates to substituted cyclopentenones has been studied independently by two groups of investigators[49,50]. The method is used widely, employing various soluble complexes of copper iodides. This approach also permits the development of methods of synthesis of 4-alkoxycyclopentenones. (±)-PGE_1, (±)-11-deoxy-PGE_1, the corresponding $F_{1\alpha}$ and $F_{1\beta}$ derivatives, and (±)-9-oxo-13-*cis*-prostanoic acid[49] have been obtained by this procedure. The synthesis of PGE_1 is illustrated in Scheme 8.[49]

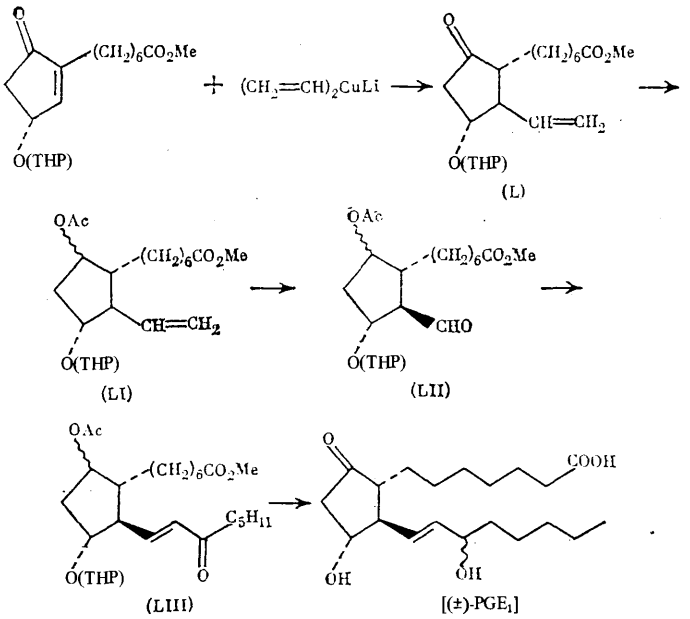
The main reaction is the coupled addition of $(CH_2{=}CH)_2CuLi$ {prepared from bis(trimethyl phosphite)copper cyanide $[(MeO)_3P]_2CuCN$ and vinyl-lithium in ethereal solution} to 4-O(THP)-2-(6'-methoxycarbonylhexyl)cyclopent-2-en-1-one with formation of (±)-vinylcyclopentanone (L) having the required steric configurations of all three asymmetric centres

Scheme 7

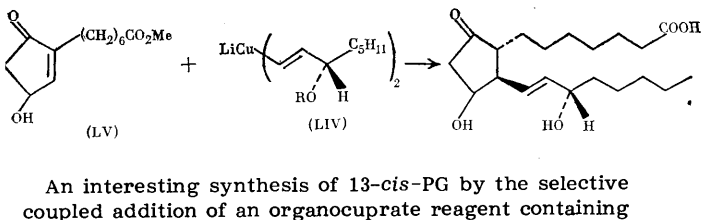


of the cyclopentane ring. The subsequent stages in the synthesis of the required PG were performed without the purification of the intermediate compounds. The reduction of the vinyl ketone (L) with sodium tetrahydroborate and subsequent acetylation with acetic anhydride yielded the C(9)-epimeric acetate (LI), whose ozonolysis led to the unstable aldehyde (LII). Its condensation with dimethyl 2-oxoheptylphosphonate yielded the α,β-unsaturated ketone (LIII). The subsequent reduction of the keto-group at C(15) with $Zn(BH_4)_2$, the alkaline hydrolysis of the ester groups at C(9) and C(1), and oxidation of the OH group at C(9) with the Jones reagent led to a mixture of (±)-PGE_1 and (±)-15-epi-PGE_1. The mixture was separated by preparative thin-layer chromatography (TLC), yielding (±)-PGE_1 (3.6%) and (±)-15-epi-PGE_1 (3.2%). (±)-11-Deoxy-PGE_1 and the corresponding $F_{1\alpha}$ and $F_{1\beta}$ derivatives were synthesised by the same procedure from other cyclopentenone derivatives.

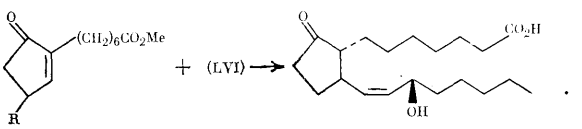
Scheme 8



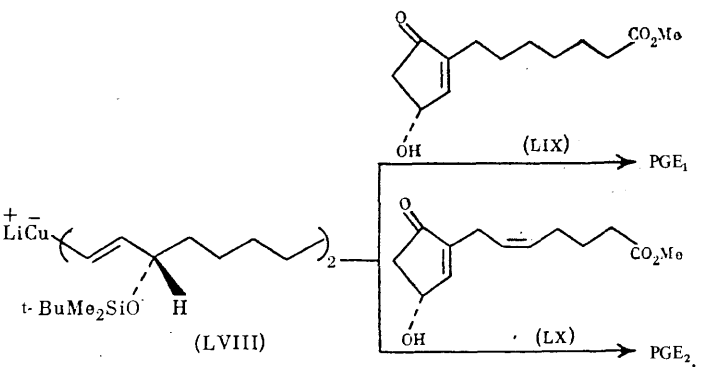
Another approach[50-61] to the synthesis of PG consists in the coupled addition of the corresponding substituted organocuprate reagent (LIV) to the enone (LV):



An interesting synthesis of 13-*cis*-PG by the selective coupled addition of an organocuprate reagent containing functional groups has been carried out[62]. It has been established that *cis*-LiCu[CH=CHCH(C_5H_{11})OC(Me)$_2$.OCH_2]$_2$ (LVI) gives rise to high yields of 1,4-adducts with a high degree of stereoselectivity, in contrast to the *trans*-isomer. Thus the interaction of compound (LVI) and 4-R-2-methoxycarbonyl-hexylcyclopent-2-enone (R=H) leads to the racemic 11-deoxy-13-*cis*-PGE_1 after mild hydrolysis (with 20% CH_3COOH). The interaction of compound (LVI) with compound [LVII, R=OC(Me)$_2$OMe] under the same conditions results in the formation of *dl*-11-hydroxy-13-*cis*-PGE_1:

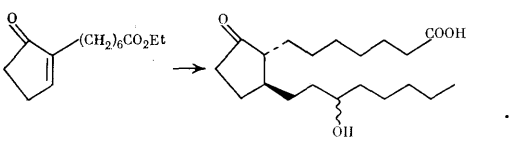


The bio-organic asymmetric synthesis of (−)-PGE_1 and (−)-PGE_2,[63-65] carried out by the coupled addition of organocuprate derivatives (LVII) [obtained from *trans*-3(*S*)-hydroxy-1-iodooct-1-ene] to the enones (LIX) and (LX) respectively may also be of interest:



It is noteworthy that the chiral centres in the key synthons (LIX) and (LX) were produced with the aid of microbiological enzymes. Different microbiological oxidation and reduction methods were used to convert the prochiral substances into optically active prostaglandin synthons. The microbiological reactions have been discussed and compared with the corresponding non-enzymic reactions used in the total synthesis of PGE_1 and PGE_2.[51]

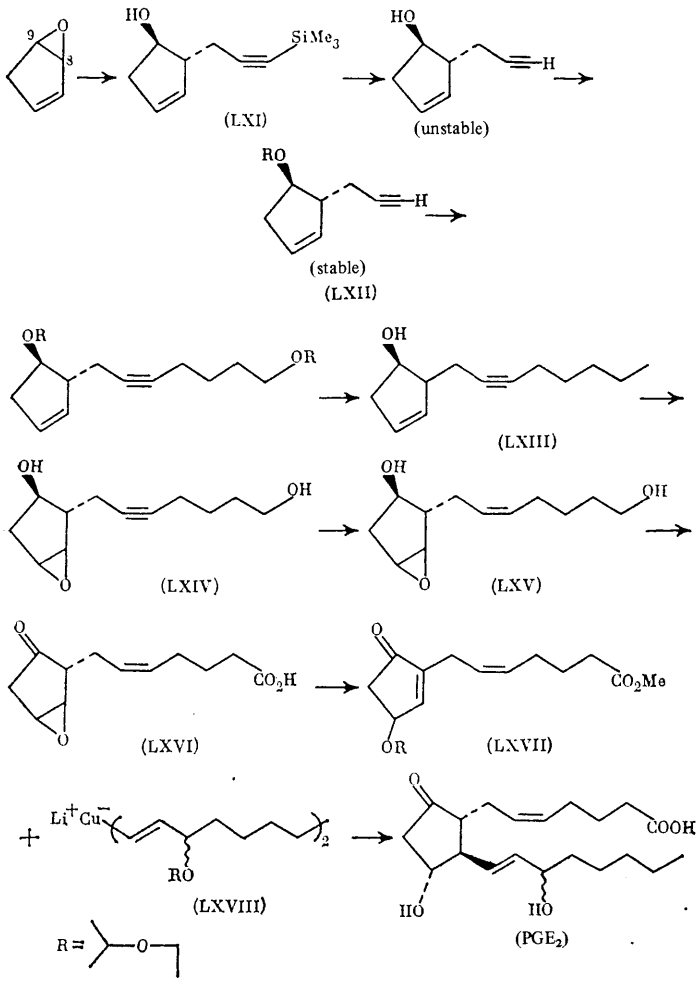
In connection with the synthesis of the racemic 11-deoxy-13-dihydro-PGE_1,[66-68] the coupled addition of t-butoxy-1-octylmagnesium bromide to 2-(6'-ethoxycarbonylhexyl)-cyclopent-2-en-1-one in the presence of Cu(I)I.PBu_3 has been described:



A general method of synthesis for 4-hydroxycyclopentenes—convenient key compounds for the direct synthesis of the PGE series—has been developed[69-71] (Scheme 9). The reaction of the epoxide derived from cyclopentadiene with the lithium salt of trimethylprop-1-ynylsilane leads to *trans*-2-(prop-2-ynyl)cyclopent-3-enol (LXI), whose interaction with ethyl vinyl ether results in the formation of the α-ethoxyethyl ether (LXII). The lithium salt of the latter is alkylated by the α-ethoxyethyl ether of 4-bromobutanol followed by the removal of the protecting groups and the formation of the diol (LXIII). The double bond of the diol (LXIII) is oxidised to the epoxy-group in (LXIV) and, after hydrogenation over 5% $Pd/BaSO_4$ in the presence of traces of quinoline, the *cis*-olefin (LXV) is obtained, its hydroxy-group being oxidised by the Jones reagent to give compound (LXVI). The epoxy-ring in compound (LXVI) is opened by successive treatment with triethylamine and trichloroacetaldehyde to

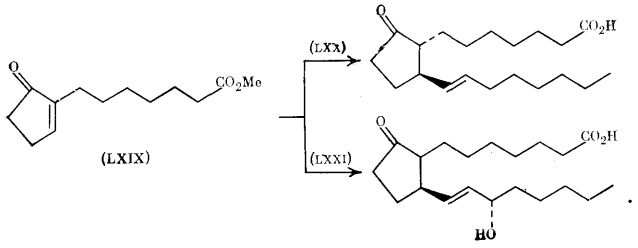
give compound (LXVII). The coupled addition of the lithium dialkylcuprate (LXVIII) (obtained from the ethyl ether of *trans*-1-iodo-oct-1-en-3-ol) to compound (LXVII) leads to a mixture of the C(15)-epimers of PGE_2.

Scheme 9



It is noteworthy that the conversion of epoxycyclopentanones (LXVI) into 4-hydroxycyclopentenones requires specific conditions for the opening of the epoxy-ring and for this reason their practical employment in the synthesis of PG is limited.

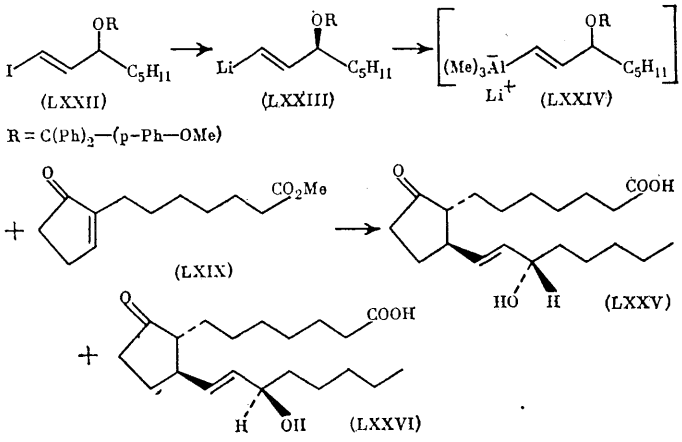
A preparatively significant synthesis of an important intermediate in the preparation of PG, namely 2-(ω-methoxycarbonylhexyl)cyclopent-2-enone (LXIX), and its single-stage conversion into the prostane skeleton have been described[72]. Octa-1,7-diene has been hydroborated by the Brown method (B_2H_6 in THF, I_2, NaOH, and HCl in aqueous THF) to form 8-iodo-oct-1-ene, from which a Grignard reagent was prepared. The latter reacts with 2-methoxycyclopent-2-enone, forming 2-(oct-7-enyl)cyclopent-2-enone. This ketone is oxidised in succession by *m*-$ClC_6H_4CO_3H$ and then H_5IO_6 to give the corresponding aldehyde, which is oxidised by the Jones reagent to the acid from which the ester (LXIX) is obtained. The reaction of compound (LXIX) with *trans*-$C_6H_{13}CH{=}CHLi$ (LXX) in the presence of $n\text{-}Bu_3PBuI$ and subsequent hydrolysis led to the formation of *dl*-11,15-dideoxy-PGE_1 in 75% yield relative to compound (LXIX). When compound (LXIX) is treated with (3*S*)-*trans*-$MeCH(OEt)OCH(C_6H_{11})CHCHLi$ (LXXI), equal amounts of 11-deoxy-PGE_1 and 11-deoxy-15-epi-PGE_1 are formed:



Like other organometallic reagents, alanates and alanes are capable of 1,4-addition to 4-alkoxycyclopentenones[73-76]. Lithium alanates are obtained from alanes by the reduction of 3-alkoxyacetylenes, the reaction usually proceeding with a 40% yield and leading to an olefin having the *cis*-configuration. However, when the alcoholic protective group at the C(15) atom is bulky, only the *trans*-olefin is formed. The simplest method of synthesising the alanate reagent involves the reaction of *trans*-vinyl-lithium with R_3Al.

A method of synthesis of 11,15-dideoxy-PGE_1, the corresponding E_2 and $F_{1\alpha}$ derivatives, 11-deoxy-PGE_1, and PGE_1 by the stereospecific coupled addition of lithium *trans*-1-alkenylalanate to the α-alkylated cyclopentene ring has been proposed[73] (Scheme 10):

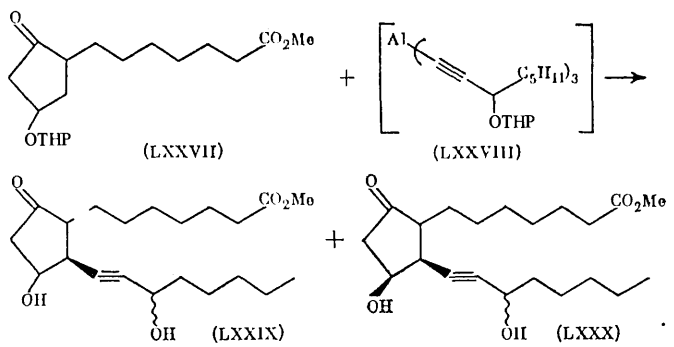
Scheme 10



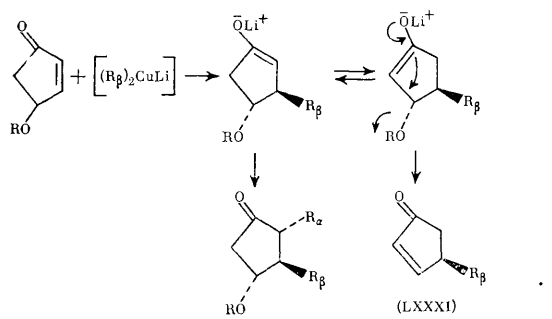
The protected 1-iodo-*E*-oct-2-en-3-ol (LXXII), obtained from the corresponding acetylenic derivative, is metallated by n-BuLi to compound (LXXIII), whose treatment with trimethylaluminium leads to the lithium alanate reagent (LXXIV). The coupled addition of the alanate (LXXIV) to the cyclopentenone (LXIX) leads, after chromatographic separation, the removal of the protective group, and hydrolysis, to *dl*-11-deoxy-PGE_1 and its C(15)-epimer (LXXVI) in proportions of 44:56 respectively.

Alanes also add to 4-alkoxycyclopentenones[77,78] with formation of PG. The reaction of the key compound (LXXVII) with tri(3-tetrahydropyranyloxyoct-1-ynyl)aluminium (LXXVIII) results in the formation, after hydrolysis and chromatography on silica gel, of the methyl ester of (±)-11β, 15(*RS*)-dihydroxy-9-oxoprost-3-ynoic acid (LXXIX) and the methyl ester of (±)-11β, 15(*RS*)-dihydroxy-9-oxo-8-isoprost-13-ynoic acid (LXXX) (Scheme 11):

Scheme 11



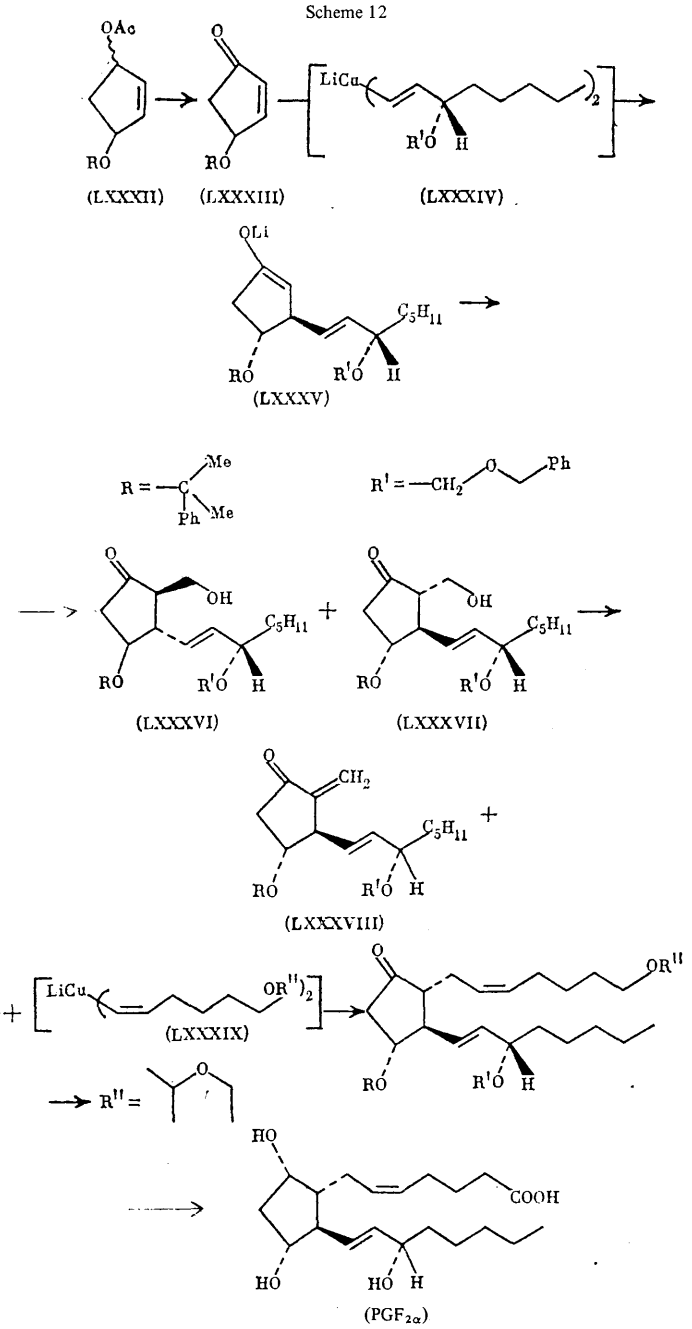
The 1,4-addition of the β-chain to 4-alkoxycyclopent-2-enone and the trapping of the resulting enolates with a finished α-chain or a potential α-chain may be regarded as one of the simplest approaches to the synthesis of PG and one involving a small number of stages. The β-chain is added in the *trans*-position of the C(11)-alkoxy-group by the Michael reaction and the subsequent trapping of the enolate leads to the complete *trans*-orientation of the three substituents in the cyclopentane ring. The main criterion of the successful application of this method of synthesis of PG is the selection of a suitable trapping agent. The low rate of trapping of the enolate of 4-alkoxycyclopent-2-enone leads to equilibrium between the enolates, which results in the elimination of the alkoxy-group with formation of the cyclopentenone (LXXXI). For example, alkylation even by reactive electrophiles, such as allyl halides, hinders only slightly the attainment of the state of equilibrium of the enolate:



An interesting solution of this problem involves the use of formaldehyde, which is an extremely reactive electrophile, in the synthesis of $PGF_{2\alpha}$ and 15-epi-$PGF_{2\alpha}$, where 4-cumenyloxycyclopenten-2-one (LXXXIII) was employed as the key compound[79-82]. The synthesis of $PGF_{2\alpha}$ was achieved in eight stages with an overall yield of 17% (Scheme 12).

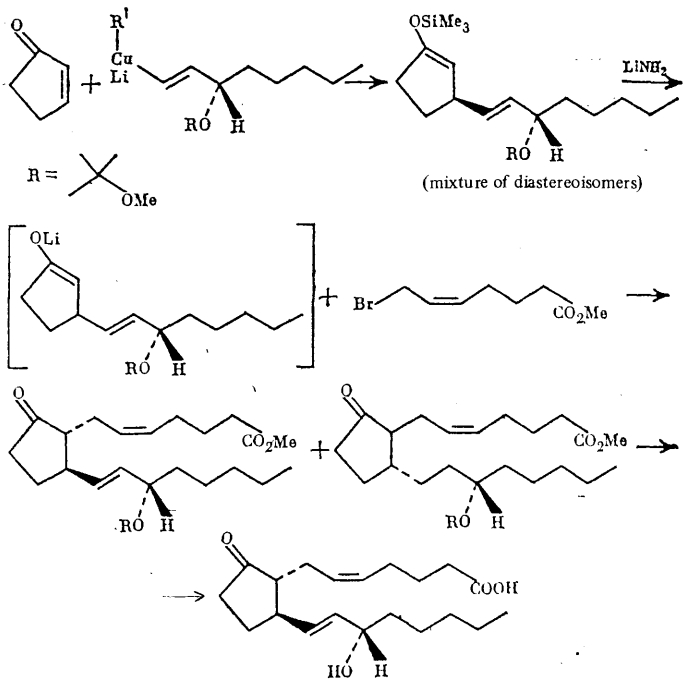
An aqueous solution of $Fe_2(SO_4)_3$ is added to cyclopentadiene, cumenyl peroxide, and $Cu(OAc)_2$ in acetic acid and 4-cumenyloxycyclopent-2-enyl acetate (LXXXII) is obtained, its alkaline hydrolysis and subsequent Jones oxidation resulting in its conversion into compound (LXXXIII). The addition of the cuprate reagent (LXXXIV) to compound (LXXXIII) in the presence of Bu_3P/CuI leads to the regiospecific enolate ion (LXXXV), whose interaction with an ethereal solution of formaldehyde produces a mixture of the alcohols (LXXXVI) and (LXXXVII) in proportions of 1 : 1.3. The dehydration of compound (LXXXVII) produces the exocyclic enone (LXXXVIII). The 1,4-addition of compound (LXXXIX) to the enone (LXXXVIII), the successive reduction of the C=O group at C(9), and the removal of the protective groups and hydrolysis lead to $PGF_{2\alpha}$, with $[\alpha]_D$ = +22.7°, and 15-epi-$PGF_{2\alpha}$.

Scheme 12



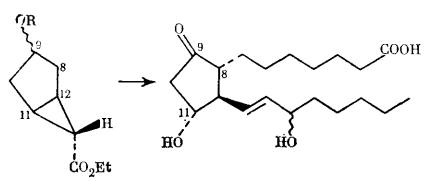
A three-stage synthesis of 11-deoxy-PGE_2 with an overall yield of 20–60%, where the β-chain was introduced by the coupled 1,4-addition of the mixed cuprate to Δ^2-cyclopentenone and the α-chain was introduced by the alkylation of a specifically oriented enolate ion, has been developed[83] (Scheme 13):

Scheme 13



3. Synthesis Based on Symmetrical Intermediate Compounds

Just and Simonovitch[84] were the first to show that a symmetrical intermediate can be used to construct the asymmetric PG molecule:

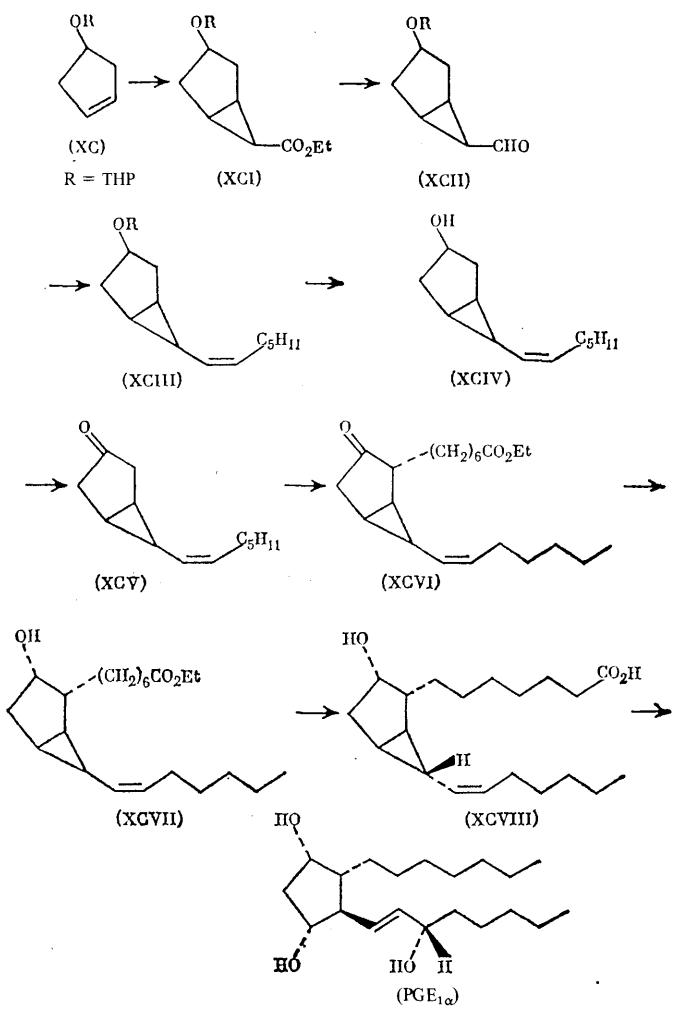


The main condition is the formation of the allyl alcohol system in the β-chain on solvolysis of the corresponding substituted cyclopropylmethanol derivative. This procedure was developed further and modified in other studies[85,86].

Scheme 14 illustrates the general method of synthesis of *dl*-$PGF_{1\alpha}$.[84] When cyclopentenol is treated with dihydropyran in the presence of $POCl_3$, the THP ether (XC) is formed quantitatively, its interaction with ethyl diazoacetate in the presence of copper powder leading to a mixture of the *syn-anti*- and *exo-endo*-isomers. When the mixture is refluxed with sodium methoxide in methanol, only the *exo*-isomer (XCI) (*syn–anti* mixture) is obtained. The ester group in the *exo*-isomer (XCI) is reduced with lithium tetrahydroaluminate to the alcoholic group (*syn–anti* mixture), which is oxidised with dilute Jones reagent to the aldehyde (XCII). The condensation of the latter with the phosphorane $(C_6H_5)_3P{=}CHC_5H_{11}$ leads to four isomers, which were separated by chromatography on Al_2O_3 with isolation of the required olefin (XCIII), whose acid hydrolysis yields the alcohol (XCIV) in the form of a mixture of four isomers, which can also be separated with the aid of TLC. The mixture (XCIV) is oxidised with a dilute Jones reagent and the resulting mixture of ketones (XCV) is also separated by TLC. The ketone (XCV) interacts with the methyl ester of 7-iodoheptanoic acid in demthylcellosolve in the presence of t-BuOK with formation of compound (XCVI), which, without being purified, is reduced with $NaBH_4$ to compound (XCVII). Alkaline hydrolysis of compound (XCVII) leads to the acid (XCVIII), a 1% solution of the latter (without purification) in 97–100% formic acid being treated with sodium carbonate, the mixture is then treated with 30% H_2O_2, the mixture of products is isolated and separated by TLC, and $PGF_{1\alpha}$ is obtained.

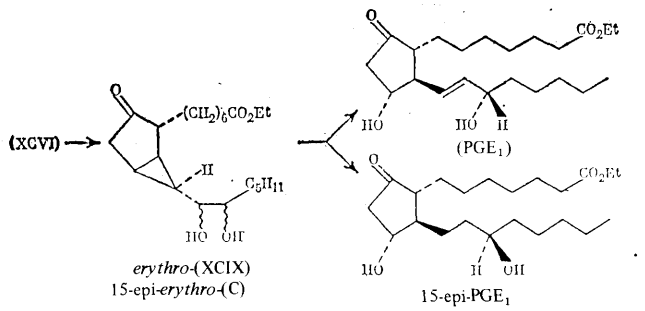
PGE_1 is obtained analogously by treating compound (XCVI) with a mixture of HCOOH and H_2O_2.

Scheme 14



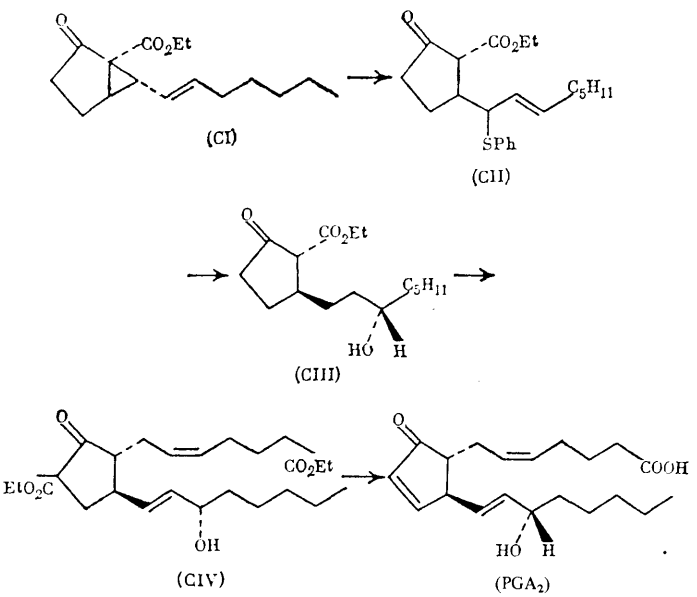
Subsequent studies showed[87–90] that, among all the approaches to the synthesis of PG via the bicyclo[3.1.0]hexane system, the best results have been obtained when the stage involving the transition from compound (XCVI) to PG was modified. Thus the hydroxylation of compound (XCVI) with OsO_4 leads to two glycols (XCIX) and (C) in approximately equal amounts[87]. The conversion of the less polar glycol (XCIX) into its bismethanesulphonate with subsequent solvolysis in a 2:1 acetone–water mixture leads to the ethyl ether of (±)-PGE_1 [17–18% relative to the glycol (XCIX)] and 19% of the ethyl ether of (±)-15-epi-PGE_1. The more polar glycol (C) produces a 19% yield of the ethyl ether of (±)-PGE_1 and a 16–17% yield of the ethyl ether of 15-epi-PGE_1.

PGE_3, (±)-PGE_2, $PGF_{2\alpha}$, and $PGF_{2\beta}$ have been obtained under the same conditions[88-90].



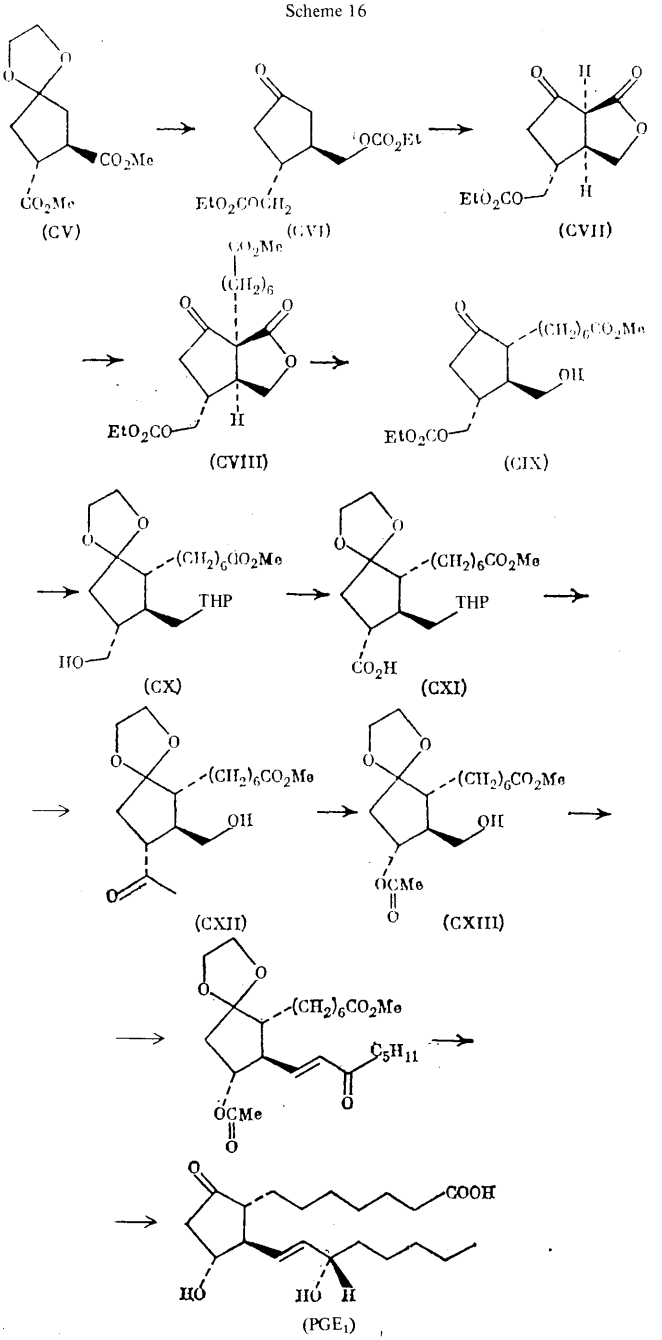
An interesting method for the opening of the cyclopropane ring has been proposed by a group of investigators[91-94]. In the stereoselective synthesis of PGA_2,[88] the cyclopropane ring in the key compound (CI) is readily opened by thiophenol in the presence of t-BuOK to give compound (CII). Subsequent oxidation with m-$ClC_6H_4CO_3H/CH_2Cl_2$ and reductive rearrangement of the sulphide (CII) by trimethyl phosphite in methanol lead to the hydroxyester (CIII). The alkylation of compound (CIII) with subsequent retro-Dieckman cyclisation give rise to the ketoester (CIV), which yields PGA_2 after hydrolysis and oxidation (Scheme 15).

Scheme 15



The syntheses of PGE_1, 11-deoxy-PGE_2, and 11α-hydroxymethyl-PGE_2 [95-97] from a symmetrical key compound, namely 3,4-dimethoxycarbonylcyclopentanone ethylene ketal (CV), obtained by the dimerisation of dimethyl maleate, has been proposed. The reduction of the ester groups in compound (CV) to alcoholic groups with $LiAlH_4$ and subsequent treatment with $ClCO_2C_2H_5$ in pyridine and then with aqueous toluene-p-sulphonic acid lead to the ketone (CVI), whose treatment with t-BuOK affords the lactone (CVII). Alkylation of the latter with methyl 7-iodoheptanoate in the presence of t-BuOK leads to the lactone (CVIII). Refluxing of compound (CVIII) in aqueous dioxan with Na_2HPO_4 and subsequent conversion into an acetal by the ethylene glycol/toluene-p-sulphonic acid mixture make it possible to obtain the corresponding hydroxyketal (CIX). Protection, alkaline hydrolysis, and transesterification with ethereal CH_2N_2 of compound (CIX) lead to the formation of the alcohol (CX), which is oxidised with CrO_3 in pyridine to the acid (CXI). On treatment with $(COCl)_2$ and condensation with Me_2CuLi, the potassium salt of the acid (CXI) is converted into the methyl ketone (CXII), whose oxidation with CF_3CO_3H/Na_2HPO_4 in CH_2Cl_2 leads to the acetate (CXIII). The latter is converted into dl-PGE_1 on oxidation of the hydroxymethyl group to the aldehyde group followed by its Wittig condensation with the corresponding phosphorane $(n\text{-}C_4H_9)_3P{=}CH{-}CO{-}C_5H_{11}$, the reduction of the oxo-group at the C(15) atom to the hydroxy-group, and the removal of the acetal protective group (Scheme 16).

Scheme 16



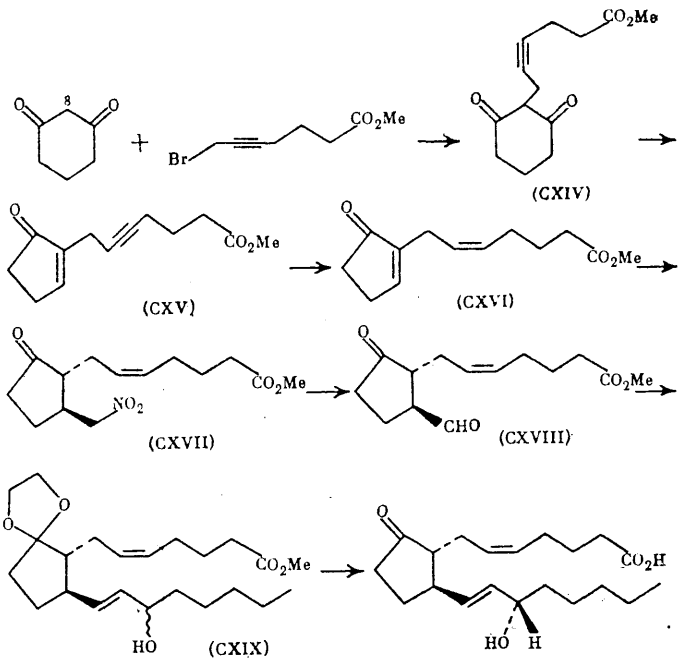
4. Synthesis Using Methods for Ring Contraction and Expansion

Bagli and Bogri[98] were the first to use the ring contraction method for the construction of the prostane ring in the synthesis of (±)-11-deoxy-PGE_1, PGE_2, and their C(15)-epimers in accordance with Scheme 17.

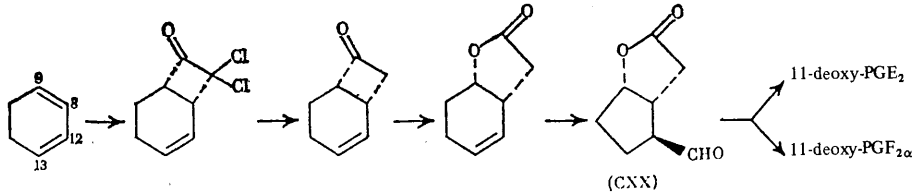
Cyclohexane-1,3-dione interacts with the methyl ester of 7-bromohept-5-ynoic acid in the presence of sodium hydride in DMF to form compound (CXIV). When the latter is treated with t-BuOCl and sodium carbonate, a rearrangement gives rise to compound (CXV), whose reduction with hydrogen (in the presence of the Lindlar catalyst) leads to the *cis*-olefin (CXVI) and the latter reacts with nitromethane in methanol in the presence of sodium methoxide to form the nitroketone (CXVII). Its treatment with sodium methoxide and subsequent hydrolysis with dilute H_2SO_4 (the Nef reaction) results in the formation of the aldehyde (CXVIII), whose condensation with the corresponding phosphonate and subsequent reduction of the C=O group at C(15) to the alcoholic group and the removal of the acetal protective group lead to 11-deoxy-PGE_2.

A similar ring contraction method was later employed to synthesise $PGF_{2\alpha}$.[99,100]

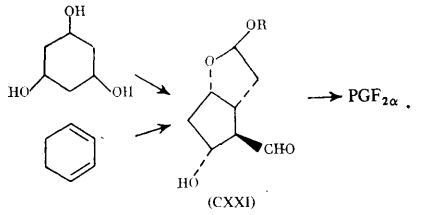
Scheme 17



Corey's approach[101] to the synthesis of 11-deoxy-PGE_2 and $PGF_{2\alpha}$ involves the contraction of the cyclohexa-1,3-diene ring and includes the following stages: (1) treatment with dichloroacetic acid in the presence of $(C_2H_5)_3N$; (2) reduction with Zn/AcOH; (3) oxidation with H_2O_2/H_2O–AcOH; (4) rearrangement under the influence of $Tl(NO_3)_3$ and oxidation with H_2O–$HClO_4$, $NaClO_4$ to the aldehyde (CXX), which is subsequently converted by standard methods into 11-deoxy-PGE_2 and 11-deoxy-$PGF_{2\alpha}$.

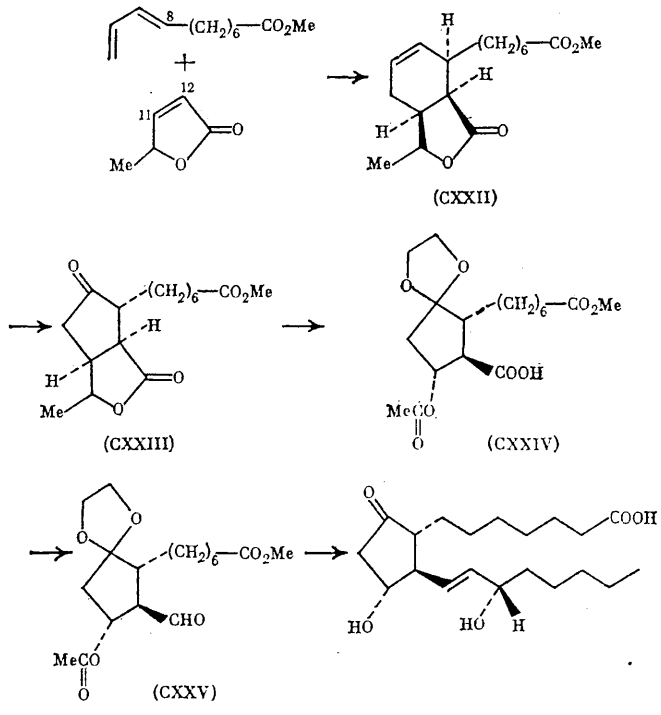


Syntheses have been described where *cis*-cyclohexane-1,3,5-triol[102] and cyclohexa-1,3-diene[103] are used as the starting materials for the synthesis of the key aldehyde (CXXI), which is readily converted into $PGF_{2\alpha}$:



An unusual solution of the problem of the synthesis of PGE_1 [104] consists in the Diels–Alder reaction between the methyl ester of undeca-8,10-dienoic acid and β-angelica lactone, leading to the *cis*-lactone (CXXII), which is oxidised with O_3 in CH_2Cl_2 and then with H_2O_2 in acetic acid to the lactone derived from the cyclopentanone (CXXIII), whose conversion into the acetal and alkaline hydrolysis lead to a lactonoacid, whose lactone ring is opened by a series of reactions to give the acid (CXXIV). It was found that the conversion of the carboxy-group into the aldehyde group without involving the methoxycarbonyl group at C(1) (Scheme 18) is impossible and the acid (CXXIV) was therefore reduced in the form of the acylimidazole derivative with $AlH(OBu\text{-}t)_3$ to the aldehyde (CXXV), which was subsequently converted by standard methods into PGE_1 in a yield higher than 50%.

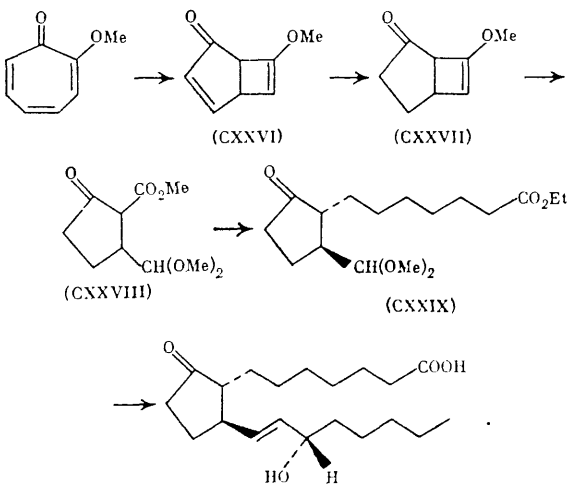
Scheme 18



The capacity of the methyl ether of α-tropolone for ring contraction on photochemical valence tautomerisation has been used successfully in the synthesis of *dl*-11-deoxy-PGE_1.[105]

The methyl ether of α-tropolone is irradiated with the light of a high-pressure mercury lamp to form 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (CXXVI), which is hydrogenated over platinum to compound (CXXVII). The latter is subjected to ozonolysis in a mixture of CH_2Cl_2 and methanol, the product is treated with liquid SO_2, and cyclopentanone acetal (CXXVIII) is obtained. The latter is alkylated with ethyl 7-iodoheptanoate in the presence of KH/DMSO with subsequent decarboxylation to the *trans*-cyclopentanone (CXXIX). The acetal group is removed and compound (CXXIX) is condensed with the corresponding phosphonate. After a series of simple operations, *dl*-11-deoxy-PGE_1 is isolated (Scheme 19).

Scheme 19

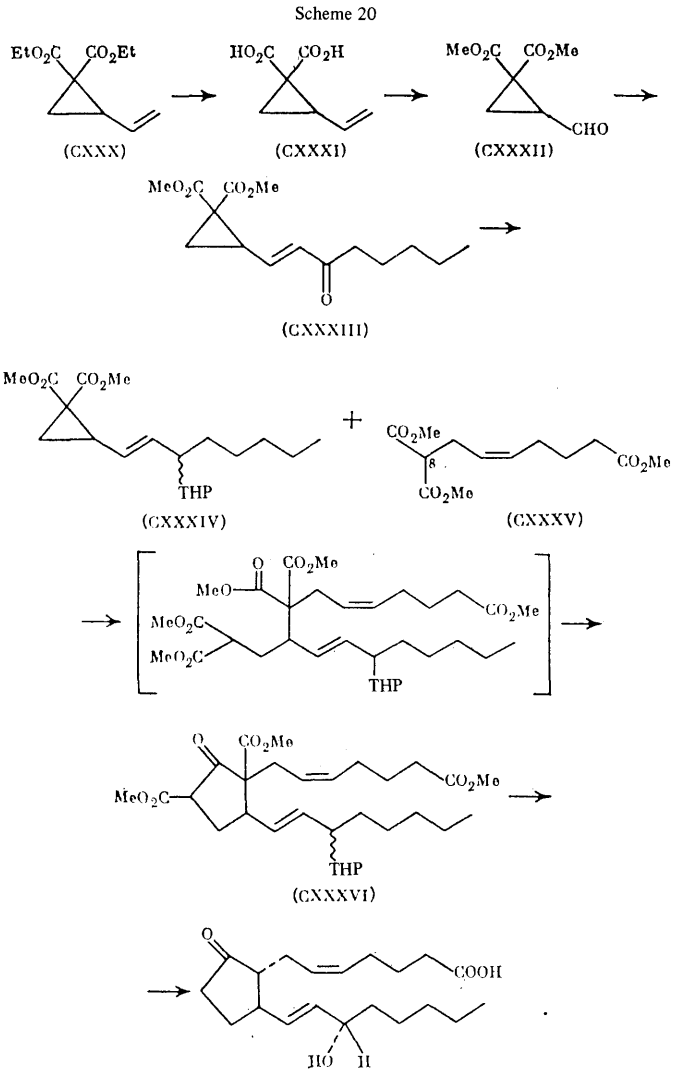


A number of syntheses of PG involve as the key stage the ring expansion reaction of cyclopropane derivatives. Thus an effective synthesis of *dl*-11-deoxy-PGE_2 and its C(15)-epimer is based on the familiar reaction in which the diethyl ester of 1-vinylcyclopropane-2,2-dicarboxylic acid (CXXX) is converted into 2,3-diethoxy-carbonyl-3-vinyl-1-cyclopentanone on treatment with sodiomalonic ester[106,107].

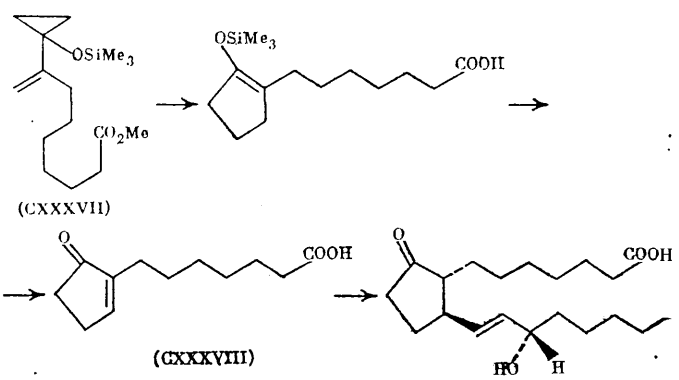
(±)-2-Vinylcyclopropane-1,1-dicarboxylic acid (CXXXI), obtained by alkaline hydrolysis from compound (CXXX), is resolved into its optical isomers with the aid of brucine; (−)-(CXXXI) is esterified with CH_2N_2 to the dimethyl ester, which is converted by ozonolysis and subsequent decomposition of the resulting ozonide with Me_2S into the aldehyde (CXXXII).

The condensation of the latter with $(MeO)_2P(O)CH_2CO.C_5H_{11}$-n leads to compound (CXXXIII), which is reduced with $NaBH_4$ to a mixture of the epimeric alcohols, whose THP ethers (CXXXIV) are allowed to react with the methyl ester of *cis*-hept-3-ene-1,1,7-tricarboxylic acid (CXXXV) in the presence of sodium methoxide with formation of compound (CXXXVI). The subsequent removal of the protective group, hydrolysis with alkali, and chromatographic separation of the epimers lead to 11-deoxy-PGE_2 in a yield up to 68% (Scheme 20):

Scheme 20



The rearrangement of the trimethylsilyl derivative of the cyclopropanol (CXXXVII) to the cyclopentanone (CXXXVIII), which is a key product in the synthesis of 11-deoxy-PGE_1, has been described[108]:



A series of new approaches to the synthesis of PG, for example, on the basis of a photochemical method, have been described in recent years[109-112]. (±)-$PGF_{2\alpha}$ has been synthesised in this way using the photolysis of a bicyclic cyclobutanone to give a γ-lactol as the key stage[109].

A synthesis of $PGF_{2\alpha}$ via carbopalladisation involving a small number of stages has been achieved[113]. The key reaction is that between cyclopentenyldimethylamine, obtained by the addition of HCl to cyclopentadiene followed by treatment with dimethylamine, and lithium tetrachloropalladate and sodiomalonic ester.

A new direct method for the conversion of castor oil into PGH_1 has also been developed[114].

However, the above approaches to the synthesis of PG have not found extensive applications.

Studies designed to obtain PG analogues, which are synthetically more readily available than natural PG and which have the same and in certain cases a higher or comparable biological activity, have been developing vigorously in recent years.

The search for synthetic analogues of PG is also dictated by other causes. In the study of the action of PG on the human organism, undesirable side effects are frequently observed (a deficiency of natural PG as therapeutic agents is the short time of their action, which necessitates frequent repeated administration of the preparations). Preparations whose structure if close to that of natural PG but which act more selectively on individual systems and functions of the organisms and are more stable, less toxic, and better tolerated by man are therefore being sought.

After the preparation of the review for publication, a number of communications on the same subject were published[115–129].

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All-Union Institute of the
Technology of Blood Substitutes
and Hormonal Preparations, Moscow

Russian Chemical Reviews

May 1984

Translated from *Uspekhi Khimii*, 53, 721-752 (1984)

U.D.C. 541.124 : 541.127

Negative Temperature Coefficient in Chemical Reactions

I.A.Leenson and G.B.Sergeev

A systematic analysis of reactions whose rate decreases with increase of temperature is presented. The possibility of a negative temperature coefficient in the elementary reactions is examined from the standpoint of the transition state theory and of collision theory. The mechanisms of complex reactions in which the temperature dependence of the rate is anomalous are discussed, and possible reasons for the anomaly are examined.
The bibliography contains 175 references.

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I. INTRODUCTION

Temperature is one of the most important factors affecting the rate of chemical reactions. The temperature range of chemical reactions in nature is very great: from a few tens of degrees Kelvin in interstellar clouds to thousands of degrees in flames, electrical discharges, etc. We need means of calculating the rates of processes at temperatures where experimental measurements are difficult or impossible. One usually assumes that if the rate constant measured at room temperature is very high (equivalent to 10% or more of the collision frequency) the activation energy is close to zero, and the rate of the reaction is almost independent of temperature. However, often this assumption is an oversimplification, and in many cases it is simply not true[1]. This can have serious consequences when attempts are made to extrapolate experimental results over a wide temperature range.

For most reactions the rate increases with temperature according to the Arrhenius equation

$$k=A\exp(-E_a/RT), \qquad (1)$$

where k is the rate constant, A is the pre-exponential factor, and E_a is the experimentally determined activation energy. However, there are many reactions whose rate decreases with increase of temperature, in obvious contradiction of the Arrhenius equation. There have been no attempts so far to discuss systematically the reactions which have a negative temperature coefficient (NTC) and to analyse the causes of the phenomenon, yet the need for such a review is urgent, both from the theoretical and from the practical point of view. Thus the rate of a reaction with a NTC could decrease very considerably on raising the temperature. A process which is predominant at moderate temperatures may be replaced (partially or fully) by competing processes with normal temperature coefficients. Conversely, a decrease in temperature should cause greater selectivity towards these reactions, and this may be important both under laboratory and under industrial conditions.

The NTC phenomenon is of interest also in astrophysics and in the physics and chemistry of the upper atmosphere, because the rate of reaction in those environments could increase by many orders of magnitude when the temperature

is lowered by hundreds of degrees[2]. Evidently, allowance for these anomalous temperature effects is needed, for example, in models of processes in interstellar clouds, of the reactions involved in the destruction of ozone in the stratosphere, etc.

Reactions with NTC are of interest also in chemical reaction theory, since many of their features are incompatible with classical chemical kinetics (collision theory and transition state theory). Therefore an analysis of these reactions could be important as a test of the theory of elementary chemical reactions, of exact or semi-empirical methods of calculating the dynamics of molecular interactions, etc.

Lastly, we note that in chemical kinetics a knowledge of the formal parameters of the rate equation (for example, the order with respect to each of the reactants) is very important in establishing the mechanism of the reaction. The detection of a NTC and the study of its origin can give valuable information on the reaction mechanism. However, it is important to remember that the NTC phenomenon could be due to the reaction itself (i.e. to its mechanism) or it could be merely a manifestation of "external" factors (an increase in the concentration of reactants caused by a decrease in temperature of the solution, the temperature dependence of the physicochemical properties of the solvent, etc.). These topics also will be discussed in this review.

A NTC was first reported for the termolecular reaction $2NO + O_2 \rightarrow 2NO_2$: together with a few similar reactions; this was treated as a rare exception, especially since the temperature coefficient was small in absolute value. However, mainly as a result of the development of sensitive new methods for monitoring the kinetics of fast reactions and of various methods for generating active species[3], the number of gas-phase reactions in which the temperature dependence of the rate is anomalous has increased in recent years. The number of reactions of this type discovered in the liquid phase and studied by traditional methods has also increased. This review will be concerned mainly with studies of the NTC published during the last 10 years, but we shall also discuss some of the older work to give the reader a more balanced view of the problem, since there are no suitable bibliographies.

II. THEORETICAL VIEWS ON THE NATURE OF THE NEGATIVE TEMPERATURE COEFFICIENT IN SIMPLE REACTIONS

1. Formal Methods of Describing the Temperature Dependence of the Rate of Chemical Reactions

In 1889 Arrhenius proposed an empirical equation to describe the temperature dependence of the rate constant of chemical reactions [Eqn.(1)]. The equation had an enormous success and became one of the fundamental equations of physical chemistry, for at least two reasons. Firstly, the vast majority of experimental data could successfully be fitted to a straight line in the Arrhenius coordinates ($\ln k$, $1/T$). As recently at the 1950's it was stated that "there are no data on unimolecular or bimolecular reactions which cannot be described by the Arrhenius equation within likely experimental error[4]". Secondly, the development of the theory of absolute reaction rates (the "activated complex" or "transition state" theory)[5] has given a clear physical meaning to the empirical parameters A and E_a.

Most of the early kinetic measurements were confined to a narrow range of temperature, for which the parameters (A and E_a) of Eqn.(1) can be treated as temperature-independent. It was difficult to encompass a wider temperature range because the conventional kinetic methods could not be used to measure rates differing by more than two orders of magnitude. For example, it was recently assumed[6] that the minimum error in the determination of the activation energy for the addition of atoms and radicals to alkenes, alkynes, and arenes in the gas phase was 4–8 kJ mole^{-1}, with a corresponding error in A between 0.6 and 1.2 litre mole^{-1} s^{-1} at 350 K. (The method of calculating mean values and standard errors of the rate constants and of their temperature dependence are discussed in Ref.7.) In many cases the reaction kinetics could be described by Eqn.(1) only because of the low precision of the determination of the rate constants and of the relatively narrow temperature range.

Improved techniques in experimental kinetics led to more precise values of the rate constants over a wider temperature range (by up to an order of magnitude). In some cases Eqn. (1) was found to apply over the extended temperature range. The "record" in this respect can be claimed by the reaction of hydrogen atoms with ethane, which obeys the Arrhenius relationship between 330 and 1350 K.[8] However, in many other reactions the Arrhenius equation was not applicable, especially in some gas-phase exchange reactions and in dissociation and recombination reactions[9]. Indeed, it has been suggested[9] that improvements in experimental techniques and theoretical developments will force us to consider not why some Arrhenius plots are curved but the very opposite problem: why so many experimental Arrhenius plots are found to be rectilinear.

The experimentally observed failure (or near-failure) of Arrhenius equation to describe various types of reaction may be due to the following factors.

1. In reactions with low or vanishingly small activation energies (or, in general, for $E_a \ll RT$) the temperature dependence of the rate constant is mainly (or even wholly) determined by the temperature dependence of the pre-exponential term A, whereas in reactions with a high activation energy the dependence of A on temperature is almost totally masked by the exponential term in the Arrhenius equation. As a result the formal application of Eqn.(1) gives a curvilinear plot, and the E_a value determined over a limited range of temperature cannot be identified with the true activation energy[10].

2) The parameter A in Eqn.(1) is not constant over a wide range of temperature, introducing a curvature into the plot of $\ln k$ against $1/T$ for any activation energy. This problem is reviewed in detail for reactions in the gas phase in Ref.9, and more generally in Ref.11, which discusses the temperature dependence of the "experimental" activation energy.

3) The Arrhenius equation assumes that the temperature of the system is uniquely defined and can be measured during the reaction. This assumption is valid if the translational and rotational degrees of freedom of the molecules are in equilibrium (or nearly so), i.e. if T is the thermodynamic equilibrium temperature. In real systems this condition is not always met, especially in the reactions taking place at high temperatures behind the front of a shock wave, in an electric arc, etc. At low temperatures deviations from the equilibrium distribution are found in fast reactions, for example in some reactions between ions and neutral molecules[12]. In these cases the rate of the process is a function of the quantum states and of the velocities of the reacting particles, and a special approach is needed[13].

In a wider range of reactions the formal application of Eqn.(1) leads to negative values of the activation energy E_a, from −1 to −40 kJ mole^{-1} or more. The statistical interpretation of the activation energy as the difference between the average energies of the activated and of the non-reacting molecules[14] formally allows the activation energy to be

negative. However, it is almost inconceivable that the activated molecules could contain less energy than the non-reacting molecules, since the activation process consists in raising the energy of a particle with respect to its normal state[15]. For this reason many workers have stated (in different ways) that a negative activation energy is physically meaningless, at least in the case of an elementary bimolecular reaction[1,2,15–19]. It is therefore preferable to use the concept of a NTC than to attempt to define a negative activation energy.

The failure of the Arrhenius equation to describe an increasing number of systems has stimulated a search for other mathematical relationships between the rate constant and the temperature of reactions. The best known is the three-parameter equation[20]

$$k=AT^n \exp(-E_a/RT) \qquad (2)$$

or

$$\ln k=A'+n \ln T-E_a/RT, \qquad (2a)$$

The three-parameter equation is theoretically justified[11] (the collision theory giving $n = 1/2$ and the transition state theory giving $n = 1$), but its application requires very precise measurements of the rate constants over a wide temperature range[7].

A simplified form of Eqn.(2) is often used for reactions with small, zero, or "negative" values of the activation energy:

$$k=A(T/T_0)^n , \qquad (3)$$

where T_0 is an arbitrary fixed temperature (for example, 298 K). In reactions with a NTC the parameter n is negative in Eqns.(2) and (3). In many systems a linear plot of $\ln k$ against $\ln T$ was obtained by Eqn.(3) over a wide range of temperature (up to 500 K), whereas in Arrhenius coordinates the plot was not linear[2].

A four-parameter $k(T)$ dependence has also been proposed[21] ($k = A \cdot \exp(-B/T) + C(T/T_0)^n$), as well as a polynomial in powers of temperature[11]. However, these equations have not been widely used, partly because of their excessive formality and partly because of the difficulties encountered in determining their parameters exactly and interpreting them physically.

Some workers have used an alternative presentation of their results: for example, by Eqns.(1) and (3) simultaneously. Often the same experimental data are described equally well by different types of equation. As an example we may quote a series of gas-phase reactions involving the t-butyl cation, which were shown[22] to obey Eqn.(3) with $n = -3$ between 190 and 570 K. In order to establish the extent to which the validity of Eqn.(3) excludes Eqn.(1), i.e. the existence of an activation energy, the authors[22] re-calculated their results by Eqn.(2a) for different assumed values of E_a, and for each E_a they chose the value of n which gave the best agreement with experiment. For $E_a > 8$ kJ mole^{-1} agreement could not be obtained with any combination of the parameters, but for $E_a = 8$ kJ mole^{-1} agreement was obtained with $n = -6$. This means that if these reactions have an activation energy it must be small. The choice of the correct equation for the temperature dependence of the rate constant is relatively unimportant for interpolation of experimental data within the experimental temperature range, but it becomes important if the data have to be extrapolated over a wider range of temperature.

2. The Negative Temperature Coefficient in the Transition State Theory

The theory of the transition state was developed for bimolecular gas-phase reactions[5]. Various mechanism are possible for the elementary act of bimolecular reactions (rebound, direct dislodgment, stripping, or pick-up)[23,24]. In the transiton state theory only a rebound mechanism of the A + BC → [A...B...C]$^{\neq}$ → AB + C type is usually considered. Let us examine the possibility of a NTC in a reaction of this type.

We should note first of all that a NTC is unusual in an elementary bimolecular reaction[25]. Most bimolecular processes have a significant activation energy, i.e. the temperature dependence of the reaction rate is determined by the exponential term in the canonical equation of the transition state theory:

$$k = \kappa \frac{k_B T}{h} \left(\frac{Q^{\neq}}{Q_A Q_B}\right) e^{-\frac{E_0}{RT}} , \qquad (4)$$

where κ is the transmission coefficient of the activated complex through the energy barrier E_0, k_B is Boltzmann's constant, h is Planck's constant, and $Q^{\neq}$, Q_A, and Q_B are the full partition functions for the activated complex and the initial reactants. If $E_0 \gg RT$ the temperature dependence of the pre-exponential term can be ignored. In the opposite limit ($E_0 \ll RT$) the temperature dependence of the reaction is determined by the ratio of the partition functions. In intermediate cases ($E_0 \cong RT$) both terms make a contribution, and a more complex temperature dependence of the reaction rate can be expected.

In the transition state method any inaccuracy in the choice of the activation barrier has a much stronger effect on the calculated rate constants than the uncertainty in the geometric parameters of the activated complex, which are used to calculate the partition functions. Therefore the transition state method is used only to calculate the pre-exponential factor in the Arrhenius equation[24]. Let us consider the cases in which a NTC can be expected, and its likely magnitude.

Obviously, a NTC in a bimolecular reaction can be expected only through the temperature dependence of the pre-exponential term in Eqn.(4), which is determined by the ratio of partition functions on the assumption that $\kappa = 1$. Usually the contribution from nuclear and electronic terms can be ignored, and the translational, rotational, and vibrational partition functions per degree of freedom can be expressed by the equations[5]

$$q_t = (2\pi m k_B T)^{1/2}/h, q_r = (8\pi^2 I k_B T/\sigma h^2)^{1/2},$$

and

$$q_v = [1 - \exp(-h\nu/k_B T)]^{-1}$$

It follows from these formulae that $q_t \propto T^{1/2}$ and $q_r \propto T^{1/2}$ always, whereas $q_v \propto T^0$, i.e. it is independent of temperature, for high-frequency vibrations and low temperatures ($h\nu \gg k_B T$), and $q_v \propto T$ for low-frequency vibrations and (or) high temperatures ($h\nu \ll k_B T$). Thus the result depends both on the vibration frequency and on the temperature[26]. For example, at 80 K $q_v \cong 1$ for practically all the frequencies of molecular vibrations, whereas at 300 K $q_v = 1.0000005$ for $\nu = 3000$ cm^{-1}, 1.008 for $\nu = 1000$ cm^{-1}, and 1.097 for $\nu = 500$ cm^{-1}, so that the error caused by assuming $q_v \cong 1$ is greater than 10% only for frequencies lower than 500 cm^{-1}. In molecules of moderate complexity the number of low-frequency vibrations is small, and therefore the q_v value begins to deviate significantly from 1 only at high temperatures, where the condition $k_B T \ll h\nu$ is not satisfied.

The ratio $Q^{\neq}/Q_A Q_B$ has been determined[27], together with the temperature dependence of the pre-exponential, for some bimolecular reactions with different configurations of the reactants in the activated complex. It was assumed in the calculations that the formation of the activated complex is

accompanied by the loss of three translational degrees of freedom in one of the reactants and by the appearance of new vibrational degrees of freedom, including one in the direction of the reaction coordinate. This low-frequency vibration is responsible for the appearance of the factor k_BT/h in formula (4). It is also assumed that the reactants and the activated complex can rotate as a single entity: for example, in the reaction between an atom and a linear molecule with a linear activated complex two rotational degrees of freedom (each) from the reactants and the complex cancel.

Table 1. Temperature dependence of the pre-exponential factor A for different types of bimolecular reaction.

No.	Reactants and activated complex*	A	$A(T)$	
			$h\nu \gg k_BT$	$h\nu \ll k_BT$
1	A + A → (AK)$_{lin}$	$(k_BT/h)\,(q_t^2/q_t^3)$	$A \sim T^{1/2}$	$A \sim T^{1/2}$
2	A + M$_{lin}$ → (AK)$_{lin}$	$(k_BT/h)\,(q_V^2/q_t^3)$	$A \sim T^{-1/2}$	$A \sim T^{3/2}$
3	A + M$_{lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)\,(q_Vq_r/q_t^3)$	$A \sim T^0$	$A \sim T^1$
4	A + M$_{non\text{-}lin}$ → (AK)$_{lin}$	$(k_BT/h)\,(q_V^3/q_t^3q_r)$	$A \sim T^{-1}$	$A \sim T^2$
5	A + M$_{non\text{-}lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)\,(q_V^2/q_t^3)$	$A \sim T^{-1/2}$	$A \sim T^{3/2}$
6	M$_{lin}$ + M$_{lin}$ → (AK)$_{lin}$	$(k_BT/h)\,(q_V^4/q_t^3q_r^2)$	$A \sim T^{-3/2}$	$A \sim T^{5/2}$
7	M$_{lin}$ + M$_{lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)\,(q_V^3/q_t^3q_r)$	$A \sim T^{-1}$	$A \sim T^2$
8	M$_{lin}$ + M$_{non\text{-}lin}$ → (AK)$_{lin}$	$(k_BT/h)\,(q_V^5/q_t^3q_r^3)$	$A \sim T^{-2}$	$A \sim T^3$
9	M$_{lin}$ + M$_{non\text{-}lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)\,(q_V^4/q_t^3q_r^2)$	$A \sim T^{-3/2}$	$A \sim T^{5/2}$
10	M$_{non\text{-}lin}$ + M$_{non\text{-}lin}$ → (AK)$_{lin}$	$(k_BT/h)\,(q_V^6/q_t^3q_r^4)$	$A \sim T^{-5/2}$	$A \sim T^{7/2}$
11	M$_{non\text{-}lin}$ + M$_{non\text{-}lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)\,(q_V^5/q_t^3q_r^3)$	$A \sim T^{-2}$	$A \sim T^3$

*Symbols. A is an atom, M$_{lin}$ and M$_{non\text{-}lin}$ are linear or non-linear molecules, AK is the activated complex.

The results of the calculation and estimates of possible temperature dependences of the pre-exponential are given in Table 1. We note that an inverse temperature dependence of the pre-exponential is theoretically possible, and that the effect is most marked for reactions at moderately high temperatures involving complex molecules giving a non-linear activated complex without low-frequency vibrations, i.e. for $h\nu \gg k_BT$. Under these conditions the exponent in Eqns.(2) and (3) becomes† $n = -2$. If Eqn.(3) is used to describe the temperature dependence of the reaction rate the negative values of n obtained according to Table 1 are easily converted into "negative activation energies" by the formula $E_a = nRT$.

Thus according to the transition state theory the magnitude of the NTC should increase as the temperature increases. The maximum possible NTC at 300 K ($n = -2$) corresponds to $E_a = -5$ kJ mole^{-1}, and therefore the presence of even a small activation barrier can fully compensate the inverse temperature dependence of the pre-exponential. Hence according to transition state theory a NTC can be expected for bimolecular reactions with a small (or zero) activation energy (for example, reactions involving free radicals). From the standpoint of the transition state theory the NTC phenomenon has been analysed for the addition of OH$^\cdot$ radicals to unsaturated compounds[28,29] as well as the addition of oxygen atoms[1] and other atoms and radicals[6], and for the reaction of NO with BrO$^\cdot$ [30] and with $CH_3OO^\cdot$.[31]

† Case 10 in Table 1, which gives $n = -2.5$, is hardly likely to be realisable in practice.

The formulae in Table 1 give only an approximate estimate of the pre-exponential because of the incorrectly assumed equality of the partition functions of the reactants and of the activated complex[32]. The change in the vibrational partition functions accompanying the formation of the activated complex was allowed for in an analysis[32] of the temperature dependence of the steric factor in the expression $A = Pz$, where A is the pre-exponential terms P is the steric factor, and z is the frequency factor: it was found that for simple unimolecular reactions the parameter P is only weakly temperature-dependent. For example, in the decomposition of ethane P increases approximately 10-fold when the temperature is increased from 300 to 400 K, but the effect is completely masked by the increase of 2^{10} in the Boltzmann factor.

For bimolecular reactions the dependence of the steric factor on temperature was found to be

$$\mathrm{d}\ln P/\mathrm{d}T = -3{,}5/T - (h^2c^2/k_B^2T^3) \times \times \sum \{\nu_i^2 \exp(h\nu_i/k_BT)/[\exp(h\nu_i/k_BT) - 1]^2\} \quad (5)$$

where ν_i are the vibration frequencies, and terms in the summation appear with the "plus" or "minus" sign according to whether they refer to the reactants or to the activated complex. Thus a negative temperature coefficient of the steric factor is a characteristic feature of bimolecular reactions. In replacement reactions at $T > 273$ K the second term in formula (5) can be ignored, so that $\mathrm{d}\ln P/\mathrm{d}T = -3.5/T$, i.e. $P \propto T^{-3.5}$. The frequency factor varies with temperature according to the law $z \propto T^{1/2}$, and therefore in this type of reaction we expect $A \propto T^{-3}$.

When analysing the temperature dependence of $Q^{\neq}/Q_AQ_B$ we must also allow for possible internal rotations in the reactants and in the activated complex. Several gas-phase reactions between ions and neutral molecules have been examined from this standpoint[2,22,26,33,34]. In the expression for the ratio of the full partition functions only the q_V values corresponding to vibrational degrees of freedom unchanged by the transition from the reactants to the activated complex were retained. However, the initial molecules may have internal rotational degrees of freedom (for example, the rotation of methyl groups). The formation of the activated complex converts some of the internal rotations of the reactants into torsional vibrations of the complex, which contribute an additional term to the temperature dependence of the pre-exponential.

The following expression has been obtained[26] for the temperature dependence of the rate constant:

$$k = CT \frac{(T_t^{\neq})^{3/2}(T_r^{\neq})^{j/2}}{\prod_i (T_t)_i^{3/2}(T_r)_i^{j/2}} T_{\text{int.rot.}}^{\Delta r/2} \exp(-E_0/RT) \quad (6)$$

where C includes the temperature-independent terms, Δr is the total number of new internal rotations, i.e. the difference between the number of new internal rotational degrees of freedom in the activated complex and the number of frozen internal rotational degrees of freedom in the reactants, $j = 0$ for atom reactions, $j = 2$ for linear molecules, and $j = 3$ for non-linear molecules, and the subscript to T indicate the origin of the various temperature terms. It is assumed (to simplify the problem) that the torsional vibrations of the activated complex produced by the suppression of the internal rotations have a fairly high frequency and do not contribute significantly to the temperature dependence of the rate constant: for this reason Eqn.(6) does not include explicitly a term for this vibration. For the opposite assumption each low-frequency torsional vibration would contribute a temperature-dependent term, and in the limit of $\nu \to 0$ we would obtain the $q_V \propto T$ dependence.

The temperature dependences of the pre-exponential factor calculated with the above assumptions for bimolecular reactions of atoms and molecules with different configurations of the reactants and of the activated complex are given in Table 2. Unlike the data in Table 1, those in Table 2 show that the absolute value of the NTC depends on the complexity of the reacting molecules. Thus the maximum NTC (for negative Δr) will be observed when the largest number of internal rotations in the reactant molecules is suppressed without forming new internal rotations in the activated complex. This can be expected in rigid activated complexes: in "loose" complexes the reactants retain their rotational degrees of freedom and the temperature dependence of the pre-exponential is weak. The parameter Δr can be calculated from experimental data. Thus the temperature dependence $k \propto T^{-3}$ mentioned above for the reaction of the t-butyl ion with isopentane[22] can be compared with the equation $k \propto T^{(\Delta r - 4)/2}$ (last line in Table 2), giving $(\Delta r - 4)/2 = -3$, and $\Delta r = -2$, which corresponds to the suppression of only two internal degrees of freedom in the activated complex. At the same time if a rigid activated complex is formed in the same system up to six internal rotational degrees of freedom can be frozen, and in general the model can be used to interpret experimental data without difficulty[22].

Table 2. Temperature dependence of the pre-exponential factor for bimolecular reactions allowing for the loss of internal rotations in the activated complex.

No.	Reactants and activated complex*	$A(T)$
1	$A + A \rightarrow (AK)_{lin}$	$A \sim T^{1/2}$
2	$A + M_{lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-1)/2}$
3	$A + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{\Delta r/2}$
4	$A + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-2)/2}$
5	$A + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{(\Delta r-1)/2}$
6	$M_{lin} + M_{lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-3)/2}$
7	$M_{lin} + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{(\Delta r-2)/2}$
8	$M_{lin} + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-4)/2}$
9	$M_{lin} + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{(\Delta r-3)/2}$
10	$M_{non\text{-}lin} + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-5)/2}$
11	$M_{non\text{-}lin} + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{(\Delta r-4)/2}$

*Symbols as in the footnote to Table 1.

Let us now examine termolecular reactions in terms of the transition state method. These reactions include the recombination of atoms and simple radicals. The NTC phenomenon was observed in the recombination of halogen atoms[35–40], in the reactions $H^{\cdot} + O_2 + M \rightarrow HO_2^{\cdot} + M$ [41] and $OH^{\cdot} + NO_2 + M \rightarrow HNO_3 + M$ (where M is any third body able to take up the excess energy),[42] and also in some processes accompanied by light emission in which electronically excited particles are first formed[43]. Some reactions involving NO have also been classified as termolecular[44,45]. Lastly, the termolecular mechanism probably applies to some reactions involving ions, for example $N^+ + N_2 + He \rightarrow N_3^+ + He$;[26] many of these reactions have a high NTC (see Refs. 46–48 for experimental data on their kinetics).

In termolecular reactions the total number of participating atoms is usually small, internal molecular rotations are usually absent, and the temperature dependence of the pre-exponential factor can be calculated as in Table 1. From the formulae thus obtained (Table 3) we note that the transition state theory predicts the possibility of a NTC for any termolecular reaction. There is no energy barrier to the recombination of atoms, and therefore according to the theory we can expect a NTC for these reactions in the form of Eqn. (3), with $n = -1$ or $n = -1/2$.

Table 3. Temperature dependence of the pre-exponential factor in termolecular reactions.

No.	Reactants and activated complex*	A	$A(T)$	
			$h\nu \gg k_BT$	$h\nu \ll k_BT$
1	$A + A + A \rightarrow (AK)_{lin}$	$(k_BT/h)(q_r^2q_v^3/q_t^6)$	$A \sim T^{-1}$	$A \sim T^{2}$
2	$A + A + A \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_r^3q_v^3/q_t^6)$	$A \sim T^{-1/2}$	$A \sim T^{3/2}$
3	$A + A + M_{lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^5/q_t^6)$	$A \sim T^{-2}$	$A \sim T^{3}$
4	$A + A + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_r^4q_v^4/q_t^6)$	$A \sim T^{-3/2}$	$A \sim T^{5/2}$
5	$A + M_{lin} + M_{lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^7/q_t^6q_r^2)$	$A \sim T^{-3}$	$A \sim T^{4}$
6	$A + M_{lin} + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_v^6/q_t^6q_r)$	$A \sim T^{-5/2}$	$A \sim T^{7/2}$
7	$M_{lin} + M_{lin} + M_{lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^9/q_t^6q_r^4)$	$A \sim T^{-4}$	$A \sim T^{5}$
8	$M_{lin} + M_{lin} + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_B/Th)(q_v^8/q_t^6q_r^3)$	$A \sim T^{-5/2}$	$A \sim T^{7/2}$
9	$M_{lin} + M_{lin} + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^5/q_t^{10}q_r^5)$	$A \sim T^{-9/2}$	$A \sim T^{9/2}$
10	$M_{lin} + M_{lin} + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_v^9/q_t^6q_r^4)$	$A \sim T^{-4}$	$A \sim T^{5}$
11	$M_{non\text{-}lin} + M_{non\text{-}lin} + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^{12}/q_t^6q_r^7)$	$A \sim T^{-11/2}$	$A \sim T^{13/2}$
12	$M_{non\text{-}lin} + M_{non\text{-}lin} + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_v^{11}/q_t^6q_r^6)$	$A \sim T^{-5}$	$A \sim T^{6}$

*Symbols as in the footnote to Table 1.

A stronger temperature dependence should be observed for reactions involving complex molecules. The maximum value ($n = -11/2$) of the NTC is found in case 11 of Table 3 for a zero activation energy and no low-frequency vibrations ($q_V \propto T^0$, i.e. it is independent of temperature). However, if a reaction of this type has a small positive activation energy the rate constant will go through a maximum[5,49]. The condition for a maximum in the function $T^n \exp(-E_0/RT)$ gives $T_{max} = -E_0/nR$. The greater the activation energy for a given n, the higher the temperatures at which a NTC will be observed. For example, for $n = -5$ and $E_0 = 8$ kJ mole^{-1} the NTC will be found at $T > 200$ K. In the presence of low-frequency vibrations, when q_V increases with temperature, the NTC effect may be compensated by the contribution from the vibrational partition functions. Thus we note from Table 3 that the q_V terms appear in the numerators of the formulae for the pre-exponential factor raised to a high power, so that the positive temperature dependence will increase steeply with temperature, as shown in Table 3 by the second limiting value (when $h\nu \ll k_BT$ and $q_V \propto T$).

We can allow for the low-frequency vibrations as follows[5,49]. Consider, for example, the reaction of three linear molecules with a non-linear activated complex (case 8 of Table 3, which can be realised by the reaction between NO and O_2). For this reaction Eqn. (4) becomes

$$k = \varkappa C T^{-7/2} \left\{ \prod_{j=1}^{11} [1 - \exp(-h\nu_j/k_BT)]^{-1} \Big/ \prod_{i=1}^{3} [1 - \exp(-h\nu_i/k_BT)]^{-1} \right\} \times \exp(-E_0/RT), \quad (7)$$

where the term C includes all the temperature-independent factors, the subscripts i denote the reactants, and j denotes the activated complex, in which 1 of 12 vibrational degrees

of freedom is converted into the reaction coordinate. Eqn. (7) can be re-written

$$\frac{d}{d(1/T)} \ln \{k\Pi [1-\exp(-h\nu_i/k_B T)]^{-1} T^{7/2} / \Pi [1-\exp(-h\nu_j/k_B T)]^{-1}\} = -E_0/R \quad (8)$$

Thus a plot of the polynomial

$$\ln k + \ln \Pi [1-\exp(-h\nu_i/k_B T)]^{-1} - \ln \Pi [1-\exp(-h\nu_j/k_B T)]^{-1} + {}^7/_2 \ln T$$

against reciprocal temperature should give a straight line of slope $-E_0/R$. This approach allows us to calculate the "true" activation energy from the experimental dependence of the rate constant on temperature[49,50]. The calculation assumes a knowledge of all the vibration frequencies in the initial molecules and in the activated complex.

In termolecular reactions involving complex molecules we can allow for the internal rotations of non-linear activated complexes as was done for bimolecular reactions. For example, in case 8 of Table 3 the addition of one free rotation to the activated complex converts the $T^{-7/2}$ term into T^{-3} in formula (8). If the initial molecules are diatomic the frequencies are high enough to make the corresponding q_V values independent of temperature, leading to a simplified form[49] of Eqn.(8):

$$\frac{d}{d(1/T)} \left\{ \ln k + 3 \ln T - \ln \prod_{j=1}^{\bar{r}} [1-\exp(-h\nu_j/k_B T)]^{-1} \right\} = -E_0/R \ .$$

Thus in the framework of the transition state method the conditions for the appearance of a NTC in simple bimolecular and termolecular reactions are the following: a small or zero activation energy (the NTC can be expected mainly in fast reactions[51]), the absence of low-frequency molecular vibrations, which produce compensation of the NTC for $h\nu \ll k_B T$, and the suppression of the internal rotations of the reactant molecules without forming new internal rotational degrees of freedom in the activated complex. More detailed discussions of problems in the activated complex theory are given in Refs.52–68.

The requirements on the activation energy must be examined specifically, because the conventional expression for the rate constant does not successfully predict the temperature dependence of the rate of reactions with a small or zero activation energy[55,56]. This has been demonstrated, for example, by analysing more than 60 elementary reactions in the gas-phase photochlorination of various compounds[54]. Several workers have pointed out[58] the shortcomings of the Rice–Ramsperger–Kassel (RRK) theory, which uses a model with a fixed activated complex to calculate the partition functions of the transition state in elementary reactions of the radical recombination type[59,60]. The limitations of the standard transition state theory when applied to reactions with a low or zero activation energy stimulated the development of new methods of calculation in which the position of the activated complex on the reaction coordinate is chosen near the maximum in the free energy rather than in the potential energy[55,57], or by using empirical parameters[61,62].

We should also note that the transition state theory and its corollaries are very sensitive to the assumed structure of the activated complex, especially in the case of low-frequency vibrations[9,30]. In many cases the experimental data can be described satisfactorily (including the appearance of a NTC) by postulating a set of "reasonable" parameters for the activated complex, but in other cases the observed inverse dependence of the reaction rate on temperature can only be explained by the transition state theory by ascribing unrealistic properties to the activated complex (for example, chemical bonds stronger than those of the initial molecules[1,67]). In these cases it is always assumed that the transmission coefficient in formula (4) depends on temperature[9,68].

Great care is needed[17,44] in applying the transition state theory to termolecular reactions, since most of the formally "termolecular" reactions take place by a complex mechanism rather than in a single step. Hence many of the dependences listed in Table 3 have only a theoretical significance.

3. The Negative Temperature Coefficient in the Collision Theory

Consider the temperature dependence of the rate constant of a reaction in terms of the classical collision theory[11]:

$$k = Pz \exp(-E_0/RT) \ . \quad (9)$$

This expression allows only for the translational degrees of freedom, and the molecules are treated as hard spheres. Formula (9) shows that the classical collision theory is incompatible with the NTC phenomenon, since both the energy term and the collision factor ($z \propto T^{1/2}$) increase with temperature. The steric factor P is usually assumed to be independent of temperature. For fast reactions with small or zero E_0 values the rate is determines by the pre-exponential factor $A = Pz$. If $A \propto T^n$, where n is a small positive number, the rate constant given by the simple collision theory will vary with temperature like the transport coefficients of the system, which are usually proportional to $T^{1/2}$ (viscosity, thermal conductivity) or to $T^{3/2}$ (diffusion)[69].

The development of theoretical and of experimental methods for studying fast bimolecular reactions resulted in the insertion into the formula of a reaction cross-section which is a function of the energy of the reactants[70]. In this case the temperature dependence of the rate constant is a function not only of the temperature dependences of the frequency factor z and of the Boltzmann factor $\exp(-E_0/RT)$, but also of the dependence of the reaction cross-section on the energy of the particles, which is related to temperature. If the energy of the molecules has its equilibrium distribution, the expression for the rate constant is[71]

$$k = (\pi\mu)^{-1/2} (2/k_B T)^{3/2} \int_0^\infty \sigma(E) E \cdot \exp(-E/k_B T) \, dE \ , \quad (10)$$

where μ is the reduced mass of the two reacting molecules, E is the relative translational energy, $\sigma(E)$ is the energy-dependent reaction cross-section, i.e. the probability of a collision between two particles having the relative energy of translational motion resulting in reaction. The parameter σ is sometimes called the "excitation function": its dimensions are cm^2 $molecule^{-1}$. Eqn.(10) implies that the reaction cross-section is unaffected by the internal states of molecules.

By introducing the function $\sigma(E)$ into the collision theory it became possible to describe formally many experimental data on the kinetics of elementary reactions[72]. In reactions with a barrier $E_0 \gg RT$ the Maxwell–Boltzmann distribution "selects" for the reaction only those molecules for which the reaction cross-sections correspond to the energies of the reacting pairs near the barrier ($E \cong E_0$). In this case the number of collisions between particles with $E \gg E_0$ is negligibly small, i.e. the reaction is confined to the "tail" of the energy distribution of the molecules, and the effect of the $\sigma(E)$ function can be ignored as in the classical collision theory.

In reactions with a small or zero threshold energy E_0 the exact form of the $\sigma(E)$ dependence becomes important. In principle these dependences can be determined both theoretically and experimentally. The former method relies either on quantum-chemical calculations or on the method of classical trajectories[23,70,72], in which the classical equations of motion are integrated numerically for given interaction potentials and initial conditions.

Important advances have been made in recent years in the theoretical calculation of reaction rates by analysing the trajectories of motion of reacting species. The calculations assumed a model interaction potential: this implies constructing the potential energy surface and solving the dynamic problem of the motion of the reacting particles on this surface (for example, by using classical mechanics). In these calculations the rate constants are obtained directly from the parameters of the intermolecular interactions, and they can be used to calculate $\sigma(E)$. Calculations by the classical trajectories method have given important results (in particular, on the dependence of the reaction cross-section on the energy of the reactants), but their description of the system is at best semi-quantitative because they often rely on arbitrary initial potentials[24].

As an example of this type of calculation we shall examine the reaction $D^{\cdot} + I_2 \rightarrow DI + I^{\cdot}$.[73] The calculations suggest that the vast majority of the collisions between deuterium atoms and iodine molecules cause a transition through the col of the potential energy surface, but only 30% of the collisions lead to reaction. In the remaining collisions the heavy iodine atoms are unable to move apart even by a distance of ~0.1 Å, and the deuterium atom passing through the saddle point of the potential surface rapdily reaches the far steep side, loses energy, and "slips" back into the region of the reactants. This phenomenon is characteristic of reactions between light atoms and heavy molecules: it is due to the fact that the relative velocity of the approaching deuterium and iodine atoms is much greater than the velocity with which the two atoms move apart in the iodine molecule. It is possible that, as the velocity of approach of the reactants increases, a steadily smaller proportion of the light atoms is able to negotiate the bend in the potential surface after passing through the saddle point, and this effect could be responsible for the appearance of a NTC of the reaction rate.

Calculations of the classical trajectories for elementary bimolecular reactions between particles of similar mass indicated that even in these reactions the cross-section can fall as the energy of the colliding particles increases[74]. However, the rate of decrease of the function $\sigma(E)$ is insufficient to account for a NTC of the rate constant, because the decrease in $\sigma(E)$ with temperature is masked by the positive temperature dependence of the collision frequency[67]. On the basis of these calculations[74] it was concluded that a NTC is unlikely to be found in an elementary bimolecular reaction between neutral molecules. However, a NTC has been observed experimentally in this type of reaction[75–78]. In other reactions (for example, the reaction of ions with neutral molecules) the possibility of the function $\sigma(E)$ decreasing fast enough with increase of E to cause a NTC of the reaction rate cannot be excluded. Further calculations with more precise interaction potentials are needed to reach unambiguous conclusions.

The second approach to formulating the function $\sigma(E)$ is to determine it experimentally, either from molecular beam experiments[70] or by a reverse transformation of kinetic data for the rate constant[75]. Methods of calculating rate constants from a given function $\sigma(E)$ are discussed in Ref.71.

Experimental or calculated data on the function $\sigma(E)$ for specific reactions are still scarce, and we usually need to rely on a defined model. Let us analyse some models from the standpoint of the possible existence of a NTC in the corresponding reaction.

Model 1. We assume that $\sigma(E)$ is a delta-function:

$$\sigma(E)=\sigma_0 \quad \text{for} \quad E=E_0,$$
$$\sigma(E)=0 \quad \text{for} \quad E \gtrless E_0,$$

i.e. that the reaction can take place only at the reactant energy E_0.[1] In this case we obtain from Eqn.(10)

$$k=(\pi\mu)^{-1/2}(2/k_B T)^{3/2}\sigma_0 E_0 \exp(-E_0/k_B T),$$

and if the activation barrier is small the temperature dependence is determined by the term $T^{-3/2}$. This model is not likely to apply to a real system because it is difficult to see how a reaction could be confined to a single value of the energy of the reactants (or even to a narrow band).

Model 2. Expressing the function $\sigma(E)$ as[11,72]

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=C \quad \text{for} \quad E \geqslant E_0,$$

where $C = \pi(r_A + r_B)^2$, and r_A and r_B are the effective radii of the molecules, leads to the following expression for the rate constant:

$$k = 2(r_A + r_B)^2(2\pi k_B T/\mu)^{1/2}(1 + E_0/k_B T)\exp(-E_0/k_B T).$$

If the probability of the reaction is independent of the excess energy of the reactants above the threshold value we have $k \propto T^{1/2}$ for $E_0 \ll k_B T$, and for $E_0 \gg k_B T$ the temperature dependence of k is determined by the term $T^{-1}\exp(-E_0/k_B T)$, and stays positive because of the rapid increase of the Boltzmann factor with temperature.

Model 3. This is a more realistic model, in which the reaction cross-section depends on the energy of the reactants. One of the simplest of these models assumes that the reaction between the reactants (represented as hard spheres) takes place when the relative energy of the particles along the collision line exceeds the threshold value E_0, and that the reaction cross-section increases to a limiting value of $C = \pi(r_A + r_B)^2$ as the energy increases above the threshold[9,24,72,77]:

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=C(1-E_0/E) \quad \text{for} \quad E \geqslant E_0.$$

It is assumed that the barrier is surmounted only by virtue of the relative energy of translational motion, and that the reaction probability is independent of the way in which the vibrational energy is distributed in the molecules. In this case Eqn.(10) becomes

$$k=2(r_A+r_B)^2(2\pi k_B T/\mu)^{1/2}\exp(-E_0/k_B T),$$

giving the classical formula of the collision theory. This is formally analogous to an Arrhenius with an activation energy $E_a = E_0 + RT/2$. This model gives a poor description of processes with energies near the threshold, or with very large energies[9].

So far we have examined models in which the reaction cross-section increases with the energy of the reacting molecules, or stays constant. Experiments with crossed molecular beams have shown that in many reactions $\sigma(E)$ increases from zero at some threshold energy E_0 and rapidly reaches a maximum before falling again. Obviously, a decrease in the probability of reaction as the energy of the molecules increases can lead to a NTC. Let us examine the models of the reaction cross-section which allow for the possibility of a decrease of $\sigma(E)$ with increase of E.

Model 4. In reactions with a small or zero activation energy the dependence of the cross-section on energy takes the simple form[11,72,75]

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=CE^n \quad \text{for} \quad E \geqslant E_0,$$

where C = const. This type of dependence is found, for example, in reactions of molecules with ions, where in most cases $n = -0.5$ ("Langevin cross-section", which never

leads to a non-equilibrium distribution of the molecular velocities[80]). In general this model gives a complex expression for the rate constant and the experimental activation energy E_a.[72] For integral and half-integral values of n the expressions become simpler and can be formulated analytically or tabulated in the usual way. If the reaction has no threshold energy ($E_0 = 0$ and $\sigma(E) = CE^n$) we have $E_a = 0$ for $n = -0.5$ and $E_a < 0$ for $n < -0.5$, i.e. we have a NTC.[75] The steeper the decrease of $\sigma(E)$ with temperature, the greater is the NTC. For example, for $n = -1.25$ a $k \propto T^{-0.17}$ dependence was found[75], and for $n = -1.5$ the dependence was $k \propto T^{-1}$. Plots of E_a against temperature for different values of n are given in Ref.72.

Model 5. The cross-sections of many reactions between neutral molecules can be fitted to the function[11,72]

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=C(E-E_0)^n\cdot\exp[-m(E-E_0)] \quad \text{for} \quad E\geqslant E_0,$$

where C = const, and m, $n > 0$. The presence of an exponential term ensures that as the energy E increases, the function $\sigma(E)$ goes through a maximum at $E = E_0 + n/m$, and then decreases again at a rate determined by the parameter m. In general the dependences of k and E_a on temperature are also complex, and therefore we shall limit the discussion to a few special cases. Thus for $m = n = 0$ the model reduces to model 2. If $m = 0$ the function $\sigma(E)$ can only increase with E, and in this case a NTC is not observed. If $m \neq 0$, E_a is always negative at high enough temperatures, and for $m \gg 0$ the function $\sigma(E)$ approaches the delta-function of model 1. Under these conditions $E_a = E_0 - 3RT/2$. Lastly, if the threshold energy is high enough ($E_0 \gg RT$) we have $E_a \cong E_0 + RT(n - 1/2)$, and only a positive and weakly temperature dependent activation energy can be expected. In the opposite limit, when the threshold energy is zero, $\sigma(E) = CE^n\cdot\exp(-mE)$, and the activation energy is always finite and temperature-dependent: $E_a = RT(n + 1/2) - m(n + 2)(RT)^2/(1 + mRT)$. If $mRT \gg 1$ a NTC is observed: $E_a = -3RT/2$.

Model 6. This model is similar to model 5, and is used to describe reactions between hard spherical molecules: in contrast to model 3, we put $\sigma(E) \to 0$ for $E \to \infty$:[11,72]

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=C[(E-E_0)^n/E]\exp[-m(E-E_0)] \quad \text{for} \quad E\geqslant E_0$$

where C = const. Model 3 is therefore a special case of model 6, for $n = 1$ and $m = 0$.

The general expression for the rate constant is very complex in this model, and the activation energy is $E_a = E_0 + RT(n - 1/2) - m(n + 1)(RT)^2/(1 + mRT)$, so that the observed activation energy can be both positive and negative.

All these models can lead to unexpected results, incompatible with the classical collision theory. For example, in model 6 with $m = 0$ and $n \gg 1$ at high temperatures the activation energy can be much higher than the threshold energy, so that E_a becomes temperature-dependent. For $m \neq 0$, when the function $\sigma(E)$ goes through a maximum, the activation energy at high temperatures is always negative. This form of the function is especially important in reactions with a low threshold energy E_0, because in this case the NTC phenomenon is observable even at intermediate temperatures. For reactions with $E_0 = 0$ model 6 gives $\sigma(E) = CE^{n-1}\cdot\exp(-mE)$, which is essentially the same as the corresponding expression for model 5. The compatibility of model 6 with the Arrhenius equation and the reality of the various n values are discussed in Ref.79.

In the last three models the reaction probability decreases as the energy increases. This is because both the translational and the internal energy of the colliding particles contribute to the reaction[2,81]. For example, the probability of the reaction K + HCl → KCl + H decreases almost 2-fold for a one-quantum increase in the rotational angular momentum with J = 1–4.[82]

The physical significance of the form of the function $\sigma(E)$ in models 4–6 can be inferred from the relationship between the absolute value of the threshold energy E_0 and the activation energy of the reaction. By inserting into the equation $E_a = RT^2(\mathrm{d}\ln k/dT)$, which follows from Eqn.(1), the value of k given by Eqn.(10) we find that the activation energy of the reaction is the difference between the average energy of the collisions leading to reaction and the average energy of all the collisions between pairs in the system[14,75]: $E_a = \bar{E}_{\text{reac}} - \bar{E}$. As we have already pointed out, in most bimolecular reactions with a large threshold energy E_0 a very small fraction of all the molecules (those in a "tail" of the energy distribution) is able to react, and we can only observe the rising branch of the $\sigma(E)$ function. Under these conditions $\bar{E}_{\text{reac}} > \bar{E}$, and the activation energy is positive. On the falling branch of the $\sigma(E)$ function (for a small or zero threshold energy) it is possible to find $\bar{E}_{\text{react}} < \bar{E}$, which formally corresponds to a negative activation energy. The physical significance of this observation is that the rate of reaction is higher for molecules whose energy is less than the average thermal energy of the molecules in the system. Increasing the temperature lowers the concentration of those molecules, and therefore it lowers the reaction rate. These effects are most marked at high temperatures.

The falling branch of the $\sigma(E)$ function is usually obtained in fast reactions (for example, in the recombination of free radicals). An interesting phenomenon is sometimes observed: a formally negative activation energy, indicating that the activation energy for the reverse process (the unimolecular decomposition into radicals) is lower than the spectroscopic dissociation energy D_0, since $D_0 = E_{\text{diss}} - E_{\text{reac}}$.[14,81,83] Expressing the temperature dependence of the recombination rate constant by the empirical relationship (3) gives $E_{\text{diss}} = D_0 - nRT$. Both phenomena (the NTC for the recombination reaction and the decrease in E_a for the reverse (dissociation) reaction) are usually observed at low pressures, and they denote the participation of the internal degrees of freedom of the molecules in the reaction. Thus the analysis of recombination reactions with a NTC relies on the theories of unimolecular decomposition for the reverse dissociation reactions: the relationship between the two processes and the development of a unified theory are specially examined in Ref.84. An analysis of the NTC in terms of the temperature dependence of the reaction cross-section has been reported[75] for the reaction between ClO˙ and BrO˙ radicals.

The analysis of termolecular reactions by the collision theory involves some fundamental difficulties. The first is that in the simplest form of the theory the reacting molecules are treated as hard spheres: in these circumstances the concept of a termolecular reaction is meaningless, since the probability of simultaneous contact between three hard spherical molecules is zero[44]. We therefore need to define more precisely what is meant by a three-body collision. For example, we could define a distance δ within which molecules are treated as colliding. The problem then becomes to calculate the probability of finding three molecules at distances not greater than δ. Alternatively we could introduce the time τ, defined as the duration of the binary collision (the life time of the quasi-molecule), and equate it (to a first approximation) to one vibration period, i.e. 10^{-13} s. The calculated frequencies of ternary collisions are 2 or 3 orders of magnitude lower than those of binary collisions[49,85,86].

This is why elementary reactions are almost invariably bimolecular: the only exceptions are the reactions which can only take place by a termolecular mechanism (for example, atom recombination reactions). As the number of participating atoms increases, the reaction adopts an "indirect" termolecular mechanism, with preliminary formation of a binary complex, and can no longer be considered to be elementary[87]. For example, instead of the reaction A + BCD + E → ABCD + E we have a two-step process, A + BCD → (ABCD)* followed by (ABCD)* + E → ABCD + E or (ABCD)* + E → AE + BCD, etc. (see theoretical analysis in Section III).

It has long been known that the simplest termolecular reactions in the gas phase (atom recombination reactions) have a NTC. This is inconsistent with the simple gas-kinetic theory of termolecular collisions, which gives[87] $k \propto T^{1/2}$. The classical collision theory is similarly unable to account for the absolute rate of these reactions, which are anomalously slow.

In the framework of the elementary termolecular mechanism the NTC phenomenon can be explained by postulating a reaction cross-section dependent on the energy of the reactants. It is usually assumed that the reaction is barrier-less, and that the function $\sigma(E)$ decreases as the temperature increases. "Head-on" collisions between three particles are very rare, and nearly all the collisions have an angular momentum, which increases with temperature. As a result, more energy is needed for the close approach, since some energy is dissipated in surmounting the rotational barrier. This lowers the effectiveness of the collisions and the probability of reaction at higher temperatures[81].

As in the case of bimolecular recombination reactions, which are associated with the reverse unimolecular dissociation reactions, termolecular reactions of the A + B + C → D + E type can be associated with the reverse bimolecular reactions D + E → A + B + C. This allows us to use one of the above models for bimolecular processes in the description of termolecular reactions, and hence to calculate their rate constants. Thus if we use model 5 for the cross-section of the bimolecular reaction we obtain four types of temperature dependence for the rate constant of the termolecular reaction[88]. The observed activation energy can be strongly temperature-dependent, and it can be either positive or negative depending on the threshold energy E_0 and on the parameters m and n of the model. For example, for $E_0 = 0$ and $0 < n \leq 1$ the rate constant has a maximum at $T = 0$ and falls monotonically to zero as the temperature rises. On the other hand if $n > 1$ with $E_0 = 0$, or if $n > 0$ with $E_0 > 0$, we have $k = 0$ at $T = 0$, after which the rate constant increases to a maximum before beginning to fall back again as the temperature is increased. In every case we can expect a NTC at high temperatures, since $k \propto T^{-3}$. The main weakness of this analysis of the possibility of a NTC in various bi- and termolecular reactions is the lack of a theoretical method of predicting reliably the form of the $\sigma(E)$ function for specific reactions.

In liquid-phase reactions the molecules react in a "cage" of solvent rather than by free collisions, as in the gas phase[89], and a "third body" is not needed to make possible a recombination reaction: the solvent can always act as the third body. For this reason it is impossible to lower the reaction cross-section in a solvent by raising the temperature.

In solutions bimolecular reactions with small activation energies are limited by diffusion, and therefore have a positive temperature coefficient of velocity. Thus, in the gas phase the recombination of perfluorinated ethyl, propyl, and butyl radicals at 297–457 K has a NTC,[90] whereas the recombination of ethyl radicals in liquid ethane at 94–154 K has a positive activation energy $E_a = +3.3$ kJ mole^{-1}, consistent with the activation energy for diffusion[91].

Termolecular processes are possible in solutions, since the solvent molecules in the "wall" of the cage can act as reactants. If the process is diffusion-limited it cannot have a NTC. On the other hand if the rate of the reaction is much lower than the rate of diffusion as a result of a large negative entropy of activation, and if the activation energy is close to zero, a NTC becomes possible, and we can use the transition state theory to express the temperature dependence of the rate constant.

Thus both the transition state theory and the collision theory predict the possibility of a NTC in elementary reaction under specified conditions. Most chemical reactions take place in a succession of steps, each of which (in theory) could have a positive or a negative temperature coefficient. The overall temperature coefficient of such reactions is discussed in the next Chapter of this review.

III. NEGATIVE TEMPERATURE COEFFICIENT IN COMPLEX MULTI-STEP REACTIONS

1. Negative Temperature Coefficient in Reactions Involving an Intermediate

The formation of an intermediate compound (complex) can lead to a NTC for the overall reaction. As in the definition of the concept of a termolecular collision we must define more precisely what is meant by a complex. It is usually assumed that if the reacting particles experience attractive forces and the energy of the reaction is not very great the reactants will form a "long-lived" intermediate compound. Direct experiments with molecular beams have shown that this does not always happen, and that reaction can take place by a direct mechanism[92]. We shall adopt as a formal criterion for the formation of a complex the ability of the reactants to remain at a mutual distance corresponding to a normal chemical bond for the duration of several rotation periods (i.e. for times of more than 10^{-12} s).[92]

In solutions the reactant molecules experience ~10^2 collisions in the solvent cage at each encounter, and therefore any encounter of a pair of reactants can be formally treated as a weak complex, A + B ⇌ AB.[85,89] For this equilibrium the rates of the forward and the reverse process and the equilibrium constant are, respectively, $w_1 = A_e[A][B]$, $w_{-1} = (1/\tau)[AB]$, and $K = A_e\tau$, where A_e is the encounter frequency and τ is the life time of the molecules in the cage.

We shall begin our analysis of the possibility of a NTC in reactions with an intermediate complex by considering the fast and reversible formation of a complex by the scheme

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AB \xrightarrow{k_p} P \quad , \qquad (I)$$

where $k_1 \gg k_p$ and $k_{-1} \gg k_p$. This type of system is often found in solutions. For example, molecular donor–acceptor complexes in solution are formed almost without activation energy at rates close to the diffusion rate. However, the rapid conversion of the complex into the product can be prevented by a large negative entropy of activation even if the activation energy of this step is small: such an entropy may arise from the need to transfer the molecular complex from a state of relatively free motion to the more rigid configuration of the activated complex during the conversion of AB into the product P. We may quote as an example the diene synthesis reaction of tetracyanoethylene with 9,10-dimethylanthracene, for which a NTC has been observed in various solvents[93].

Fast and reversible complex formation is possible also in gas-phase reactions at high enough pressures if the complex is in thermodynamic equilibrium with the initial substances. We may assume that under these conditions the termolecular complex formation reaction (in which the function of the third body is to dispose of the excess energy of the complex and to stabilise it) is kinetically of the second order (k_1 corresponds to k_1^∞ in the high-pressure limit), and the monomolecular decomposition reactions of the complex by two paths are in the first-order region (k_p corresponds to k_p^∞, and k_{-1} corresponds to k_{-1}^∞).

For [B] ≫ [A] the rate of reaction (I) is given by the expression

$$d[P]/dt = k_p[AB] = k_pK[A][B]/(1 + K[B]) = k_p\alpha[A] , \quad (11)$$

where $K = k_1/k_{-1} = K_0 \cdot \exp(-\Delta H/RT)$ is the equilibrium constant, and $\alpha = K[B]/(1 + K[B])$ is the extent to which component A is bound in the complex. The temperature dependence of the reaction rate is a complex function, determined by the activation energy E_p (positive), the enthalpy of complex formation ΔH (negative), and the concentration of the reactant B. It follows from Eqn.(11) that for $K[B] \gg 1$ (strong binding, $\alpha = 1$) $d[P]/dt = k_p[A]$, and for $K[B] \ll 1$ (weak binding, $\alpha = K[B]$) $d[P]/dt = k_pK[A][B]$. For strong binding the activation energy $E_a = E_p$ is positive; for weak binding $E_a = E_p + \Delta H$, so that the observed activation energy can be either positive (for $E_p > |\Delta H|$) or negative (for $E_p < |\Delta H|$). In the latter case the initial rate of reaction or the effective rate constant, depending on [B], will increase with temperature initially, go through a maximum at the temperature

$$T_{max} = \frac{-\Delta H}{R[\ln(-\Delta H/E_p - 1) - \ln(K_0[B])]} ,$$

and decrease at still higher temperatures. Similar results are obtained for the formation of intermediates of more complex composition (for example, AB_2): under these conditions the absolute value of the NTC may be higher than for the 1 : 1 complexes, since the enthalpy of formation is usually higher in the larger complexes[94].

In many fast gas-phase reactions we find three competing processes: decomposition of the complex into the initial substances, decomposition into the reaction products, and stabilisation of the vibrationally excited complex by collision with a third particle[2,52]:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AB)^* \begin{cases} \xrightarrow{k_p} P \\ \xrightarrow[k_m]{M} AB \end{cases} . \quad (II)$$

The stationary state condition gives

$$[(AB)^*] = k_1[A][B]/(k_{-1} + k_p + k_m[M]) .$$

The expression for the reaction rate is

$$d[A]/dt = -d[B]/dt = k_1[A][B] - k_{-1}[(AB)^*] = k_1(k_p + k_m[M])[A][B]/(k_{-1} + k_p + k_M[M]) .$$

The experimentally determined rate constant of the bimolecular reaction is a complex function of the temperature and pressure of the system:

$$k_{exper} = k_1(k_p + k_m[M])/(k_{-1} + k_p + k_m[M]) . \quad (12)$$

Let us examine some special cases of scheme (II).

1) For low pressures and short life-times of the complex we have $k_m[M] \ll k_p$, and scheme (II) becomes $A + B \rightleftharpoons (AB)^* \rightarrow P$. It follows from Eqn.(12) that under these conditions $k_{exper} = k_1k_p/(k_{-1} + k_p)$, i.e. the rate constant is independent of pressure. If the predominant reaction path is the decomposition of the complex into products ($k_p \gg k_{-1}$) we have $k_{exper} = k_1$ and we observe the "forward" reaction. The possibility of a NTC for these reactions has already been discussed. This case is met, in practice, when the activation energy barrier opposing the conversion of the complex into the product is small.

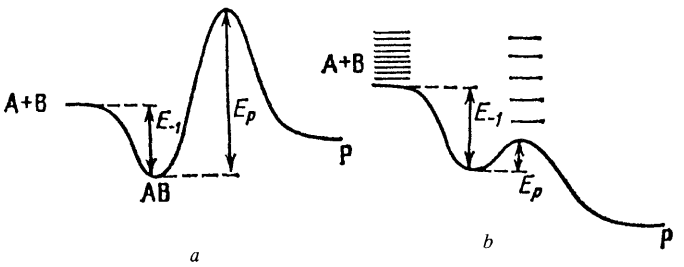


Figure 1. Energy profile of the reaction A + B ⇌ AB → P for zero vibrational level and different relative values of E_{-1} and E_p.

In the opposite limit ($k_p \ll k_{-1}$) we have $k_{exper} = k_1k_p/k_{-1}$. Since the activation barrier to the formation of the complex is usually small or zero, the temperature dependence of k_{exper} will be determined by the relative values of E_p and E_{-1}. For the temperature coefficient to be negative the energy of the activated complex for the k_p step should be lower than the energy level of the reactants ($E_p < E_{-1}$, see Fig.1). At first sight the condition $E_p < E_{-1}$ is incompatible with the condition $k_p < k_{-1}$. However, the density of energy levels for the k_{-1} reaction is much greater than the density of levels for the forward reaction (k_p) for equal internal energies (Fig.1*b*), i.e. the entropy factor strongly favours the reverse reaction and thus compensates the energy factor of the forward reaction[52,95,96]. Therefore the condition $k_p < k_{-1}$ can be satisfied even if $E_p < E_{-1}$.

In the general case ($k_p \cong k_{-1}$) the activation energy of the reaction is determined by the equation[2,97]

$$E_a = E_1 + (E_p - E_{-1})k_{-1}/(k_{-1} + k_p) ,$$

and if $E_1 \cong 0$ and $E_{-1} > E_p$ we find $E_a < 0$. This equation for E_a also shows that the absolute value of the NTC should increase with temperature, since the ratio $k_{-1}/(k_{-1} + k_p)$ increases with temperature.

Both the decomposition paths of the complex are unimolecular processes, with rate constants k_{-1} and k_p, and they can be analysed by standard methods (for example, the RRK theory[2,58,96]). The pre-exponential factors for the k_p and k_{-1} steps were calculated[67,98], and it was shown that if these factors (A_{-1} and A_p) are similar, $k_p \gg k_{-1}$, i.e. the forward reaction takes place. In order to observe the NTC associated with the reversibility of the complex formation we must satisfy the condition $A_{-1} \gg A_p$, which has been shown theoretically to be easily possible in real systems[98].

2) At high enough pressures the rate of deactivation of the complex is much greater than the rate of conversion into products ($k_m[M] \gg k_p$), i.e. scheme (II) is converted into the scheme $A + B \rightleftharpoons (AB)^* \xrightarrow{M} AB$. In this case it follows from Eqn.(12) that $k_{exper} = k_1k_m[M]/(k_{-1} + k_m[M])$; the main reaction is the association of the initial molecules A and B

into the product AB (a stable complex or molecule[28,58,99]). Stabilisation of the transition complex (AB)* usually takes place through collision with a third body, but radiative stabilisation has also been reported[58,100]. If $k_m[M] \gg k_{-1}$, we have $k_{exper} = k_1$, and we observe the "forward" reaction; if $k_m[M] \ll k_{-1}$, $k_{exper} = k_1 k_m[M]/k_{-1}$. The possibility of a NTC in these cases was discussed above.

In the general case ($k_m[M] \cong k_{-1}$) we can assume that the rate constants of the bimolecular processes k_1 and k_m are not very different from the frequency factors, and weakly dependent on temperature. Under these conditions the temperature dependence of k_{exper} will be determined by the temperature dependence of the function $1/k_{-1}$. Some workers have used the RRK theory to describe the constant k_{-1} qualitatively[2,58]: for small molecules at moderately high temperatures this gives $k_{-1} \propto T^{s-1}$, where s is the number of oscillators. Thus for small molecules $k_{exper} \propto T^{1-s}$, and if $s > 1$ this gives a NTC.[2]

Other bimolecular reaction mechanisms with formation of an intermediate complex are also possible. For example, the product may be formed from the stabilised (rather than from the excited) complex by the scheme[2] $A + B \rightleftharpoons (AB)^* \overset{M}{\rightarrow} AB \overset{C}{\rightarrow} P$. This scheme also can produce a NTC. Thus, if $[C] \ll [M]$ and $[AB] \ll [A]$ we have $k_{exper} = k_p K[M]$, whence $E_a = E_p + \Delta H$, and a NTC is observed when $E_p < |\Delta H|$, where ΔH is the enthalpy of the process $A + B \rightleftharpoons (AB)^*$.

The NTC has been attributed to the reversible formation of an intermediate complex in reactions involving atoms of oxygen and other elements of Group VI,[66,68,101,102] in the interaction between BrO· radicals[103], in the gas-phase reaction of mercury with ammonia and with hydrogen iodide[104], in proton transfer reactions of ion–molecule processes[105], and in the reactions $HO_2^{\cdot} + NO \rightarrow OH^{\cdot} + NO_2$,[106] $CH_3O_2^{\cdot} + HO_2^{\cdot} \rightarrow CH_3OOH + O_2$,[107] and $OH^{\cdot} + C_6H_5CH_3 \rightarrow$ products[108].

More complex schemes, involving several complexes[2,34], have also been used to explain experimental results.

The participation of two types of complex is postulated in many gas-phase organic reactions[33,96,109]. For example, it has been shown by the ion cyclotron resonance method that typical nucleophilic substitution reactions can be acclerated by up to 20 orders of magnitude by transition from an aqueous solution to the gas phase: this is explained by the large change in the energy profile of the reaction on changing from strongly solvated to totally non-solvated particles[109] (Fig.2). In the gas phase the approaching particles form the ($OH^- \cdot CH_3Br$) complex, which is converted into the product (with a small activation barrier) through the intermediate complex $CH_3OH \cdot Br^-$. We see from Fig.2 that under these conditions the energy profile is similar to that of Fig.1*b*. Obviously, in the gas phase the reaction should be fast, with a NTC. In an aqueous solution the reaction is slow because of the high energy barrier resulting from the difference in solvation between the reactants and the activated complex and because of the need to break down the solvation shell of the transition state. The solvation also hinders the attractive forces between the reactants and the formation of the complex.

The kinetics of a reaction in the gas phase with stepwise solvation of the reactants by one, two, etc. water molecules are discussed in Ref.109. Solvation by only two water molecules is sufficient to raise the energy barrier opposing the conversion of the complex to the level of the initial substances, or even higher (Fig.2). Thus solvation suppresses the reaction, and the NTC is replaced by a positive temperature coefficient.

In the gas phase these reactions show an effect analogous to the Polanyi–Semenov rule. A study of 22 reactions of the type of $R_1^+ + R_2H \rightarrow R_2^+ + R_1H$ (whose energy profile is shown in Fig.1*b*) has shown that the rate increases with the exothermicity of the process[33]. This effect is due to the lowering of the activation barrier in the more exothermic reactions. An even more interesting correlation is that between the parameters k and n of the equation $k = At^n$: it was found that for a fixed temperature these parameters are linearly related in a series of reactions. Therefore the slower reactions of this type have a higher NTC, and they are more strongly retarded by an increase of temperature[33].

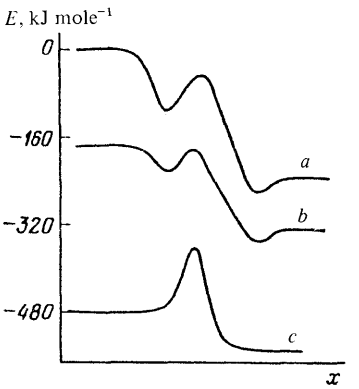


Figure 2. Energy profile of the reaction $OH^- + CH_3Br \rightarrow CH_3OH + Br^-$ for non-solvated reactants (*a*), and reactants solvated with two water molecules (*b*) or in an aqueous solution (*c*); x is the reaction coordinate.

The presence of two types of intermediate complex, mutually in equilibrium, has been suggested also for several liquid-phase reactions (for example, addition to multiple bonds[94,110]). These reactions show a NTC if the barrier to the conversion of the complex into the product is lower than the enthalpy of complex formation. The NTC phenomenon has been observed also in the gas-phase addition of hydrogen chloride to propene: in this case it was due to the reversible formation of the $(HCl)_2$ dimer and its subsequent reaction with the $C_3H_6 \cdot HCl$ complex[111].

The intermediate compound is not necessarily a complex. For example, in the scheme

$$P \overset{k_1}{\leftarrow} A \overset{K}{\rightleftarrows} B \overset{k_2}{\rightarrow} P \qquad \text{(III)}$$

A and B are isomers mutually in equilibrium, having different reactivities or different solvations. If the equilibrium is established rapidly the observed activation energy is given by the expression

$$E_a = E_1 - \frac{K}{1+K}\Delta H + \frac{Kk_2/k_1}{1+Kk_2/k_1}(\Delta H - E_1 + E_2), \qquad (13)$$

where ΔH and K are the enthalpy and the equilibrium constant for the $A \rightleftharpoons B$ process, and E_1 and E_2 are the activation energies for the conversion of A and B into the product[11]. If $|\Delta H| > |E_1 - E_2|$, for $\Delta H > 0$ and a low enough temperature ($K \ll 1$) we have $E_a = E_1$, whereas at high temperatures ($K \gg 1$) $E_a = E_2$. In either case the NTC is not observed. However, for $\Delta H < 0$ the Arrhenius dependence of the reaction rate can have several extrema, giving a NTC in some temperature ranges. Similar effects may be found in enzyme reactions when all the forms of the enzyme are present in equilibrium. Plots of the change in activation energy with temperature are shown in Ref.11.

If only one of the species reacts in scheme (III) Eqn.(13) reduces to the simpler expression $E_a = E_1 - K\Delta H/(1 + K)$ for $Kk_2/k_1 \ll 1$, or to the expression $E_a = E_2 + \Delta H/(1 + K)$ for $Kk_2/k_1 \gg 1$. In both cases a NTC can arise for certain ratios of the parameters E_1, E_2, and ΔH.

Various theories have been proposed to explain the NTC in termolecular reactions with formation of an intermediate complex (for example, the recombination of atoms and simple radicals)[81]. Most workers adopt a mechanism involving a third molecule M as well as the intermediate complex[112] (the Radical-Molecular Complex (RMC) or Intermediate Complex (IC) mechanism). If both the reactants R_1 and R_2 can form a complex with M the recombination scheme $R_1 + R_2 \rightarrow R_1R_2$ can be written, in general, as a system of many elementary steps[60,113]:

$$\begin{array}{ll} R_1 + M \rightleftarrows R_1M^* & R_2 + M \rightleftarrows R_2M^* \\ R_1M^* + M \rightleftarrows R_1M + M & R_2M^* + M \rightleftarrows R_2M + M \\ R_1M^* + R_2 \rightleftarrows R_1R_2 + M & R_2M^* + R_1 \rightleftarrows R_1R_2 + M \\ R_1M + R_2 \rightleftarrows R_1R_2 + M & R_2M + R_1 \rightleftarrows R_1R_2 + M \text{ etc.} \end{array}$$

A large number of kinetic equations is needed to describe the system fully in the general case, but far fewer equations are sufficient if $R_1 = R_2$. Even greater simplification is achieved if the equilibrium $R + M \rightleftharpoons RM$ can be assumed: in this case the recombination is third-order at low pressures and second-order at high pressures[113].

The simplified recombination scheme gives $k_{rec} = A \cdot \exp(\Delta E/RT)$ at low temperatures and $k_{rec} = A \cdot \exp[(\Delta E - RT)/RT]$ at high temperatures, where ΔE is the bond energy in the RM complex[113]. Since $\Delta E > 0$ always, we observe a NTC increasing in magnitude with the strength of the complex. For example, in the recombination of iodine atoms[44] E_a is found to vary from -5.9 kJ mole^{-1} for M = He to -22.3 kJ mole^{-1} for $M = I_2$. The complex RM is weak if M is an inert gas atom, but it can be quite strong and comparable to that in a chemical compound (for example, I–NO and I–NO_2).

Many recombination reactions have been studied over a wide range of temperature and pressure for a variety of "third molecules" (M). Heavy and complex "inert" molecules like SF_6 were found to be the most effective in recombination reactions, the NTC of the reaction increasing with the effectiveness of M. Even gases like He, Ar, and N_2 are not fully inert in practice, and they always form an RM complex[114] as well as RM_n clusters (at higher pressures[60]).

Mechanisms including the formation of an intermediate complex do not always satisfactorily describe experimental data. Thus the magnitude of the NTC is often inconsistent with the energy of the R–M bond. For example, in the reaction $I^\cdot + I^\cdot + He \rightarrow I_2 + He$ an I–He bond several times stronger than expected from the van der Waals forces had to be postulated[115]. Problems are met also in attempting to explain the temperature dependence of the activation energy of these reactions. There is no doubt that at least one more mechanism is possible for the recombination:

$$\begin{array}{l} R_1 + R_2 \rightleftarrows R_1R_2^* \\ R_1R_2^* + M \rightleftarrows R_1R_2 + M \end{array} .$$

This mechanism (Energy Transfer, or ET mechanism) competes with the formation of an intermediate complex, and it can be predominant (for example, in the NO + Cl → NOCl [116] and NO + O → NO_2 reactions[117]). This mechanism also gives a NTC, as was found above for scheme (II) with $k_m[M] \gg k_p$. In the ET mechanism the temperature dependence of the reaction rate is determined by the expression AT^n, and the observed activation energy varies with temperature ($E_a = nRT$), whereas in the intermediate complex mechanism the parameter E_a is almost independent of temperature.

The relative contribution of the two mechanisms depends on the temperature; it is difficult to extract quantitative information on the force of the R–M interaction from the temperature dependence of the recombination rate constant alone, and additional data on the dependence of k_{rec} on pressure, nature of M, etc. are needed[60]. The contribution of each mechanism depends on a number of factors: the strength of the R–M and R–R* interactions, the relative concentration of particles, and their size and complexity[87]. In the recombination of halogen atoms with M = Ar, Xe the intermediate complex mechanism is dominant at low temperatures, and the ET mechanism at high temperatures, but with M = He the latter mechanism is always predominant[114,118].

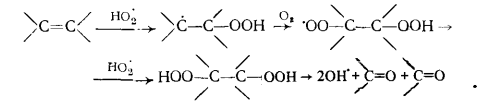
The contribution from each mechanism is harder to predict when M is a complex molecule (HCl, HBr, SO_2).[118] Keeping all other conditions the same, the relative importance of the two mechanisms is a complicated function of pressure, since clusters of M can take part in the reaction[60]. For example, in the reaction $Br^\cdot + Br^\cdot + He \rightarrow Br_2 + He$ the contribution from the ET mechanism is 40% at $p < 150$ bar and almost zero at $p > 400$ bar. In the presence of other M molecules the intermediate complex mechanism is predominant at all pressures[119]. The same is true of other reactions involving free radicals, for example $HO_2^\cdot + HO_2^\cdot \xrightarrow{M} H_2O_2 + O_2$ (M = NH_3, H_2O).[80,97,120]

2. Negative Temperature Coefficient in Gas-phase Hydrocarbon Oxidation Reactions

The oxidation of hydrocarbons is a branching chain process whose rate is a function of temperature. In most cases an increase in temperature causes a large increase in rate[121]. However, some exceptions to this rule are known. In the oxidation diagrams (in T, p coordinates) of some reactions a region in which the reaction rate decreases with increase of temperature is found above the cold flame region, i.e. a NTC is present. This NTC region lies between the low-temperature and the high-temperature oxidation region[122]. It has been suggested that the cold flame is a suppressed chain explosion which has failed to develop because of the passage of the system into the NTC zone[123].

The NTC phenomenon is observed even in the oxidation of ethane, but is more marked with the higher hydrocarbons. Thus in the oxidation of propane the reaction rate increases to a maximum in the region of 300–350 °C before falling steeply to zero when the temperature is increased to 450 °C. The reaction re-starts at 475 °C, and becomes explosive[123]. So far a NTC has been reported for the gas-phase oxidation of alkanes, alkenes, aromatic hydrocarbons, and ketones. The phenomenon is discussed in many monographs and reviews[122–126], many experimental studies have been made of it, but so far the mechanism of the NTC is not entirely clear.

Some of the early workers attributed the NTC to the presence of two parallel reactions[123], or to reactor wall effects[127]. The hypothesis of two different chain breaking mechanisms with very different activation energies was tested by kinetic calculations[128]. In the most widely used hypotheses an increase of temperature lowers the probability of chain propagation because of the presence of a competing reaction[123]. According to one of these hypotheses the NTC is due to the reaction $HO_2^\cdot + HO_2^\cdot \rightarrow H_2O_2 + O_2$, which suppresses the chain-branching reaction[124]



However, this hypothesis has been shown to be incorrect by the kinetic isotope effect method[129]. According to other interpretations a branching reaction of the type of

$(CH_3)_2CHOO^{\cdot} + C_3H_8 \rightarrow (CH_3)_2CHOOH \rightarrow CH_3CHO + OH^{\cdot} + CH_3^{\cdot}$ is replaced by a chain propagation reaction at higher temperatures[130].

It has also been suggested that in the oxidation of hydrocarbons one of the intermediate products (the aldehyde) loses its ability to cause chain branching at high temperatures[123]. The kinetics of the formation of the main intermediates and products (including free radicals) in the NTC region have been studied in detail by advanced measurement techniques[131], including continuous monitoring in a cold trap by ESR.[132,133] In the NTC region the maximum concentration of free radicals (like the reaction rate) was found to go through a maximum. However, at short times, when the branching reactions can be ignored, the concentration of free radicals in the same region increases with temperature, indicating a relationship between the NTC and the branching reactions. Thus a study of the kinetics of the high-temprature oxidation of ethane has shown that the branching steps are associated with the accumulation of intermediate products of the reaction, whereas in the initial stages a non-branching chain process is taking place[134]. The experiments also showed that in the NTC region and at even higher temperatures there was no qualitative difference in the composition of the oxidation products and only a slight quantitative difference[128]. Yet, the chain length must decrease in the NTC region, since the active radicals which propagate the chain ($H^{\cdot}$, $RO^{\cdot}$) are replaced by less active radicals as a result of the reactions between active particles and intermediate products of the HCHO and CH_3CHO type[135]. Thus the NTC in these reactions arises from a decrease in the effectiveness of chain branching at high temperatures.

3. Other Reactions

NTC have been observed also in other reactions of various types: in some cases the origin of the NTC is clear, but in other cases detailed studies of the mechanism of the process are needed to account for the effect. Thus a NTC will always be found in parallel reactions ($B \overset{k_1}{\leftarrow} A \overset{k_2}{\rightarrow} C$) if the temperature dependence of the yield of the substance formed with the lower activation energy is measured. At any instant the relationship $[B]/[C] = [B]_\infty/[C]_\infty = k_1/k_2$ applies[136]. If $E_2 > E_1$ the relative yield of the product B decreases as the temperature increases. This behaviour has been observed, for example, in the radical decomposition of azo compounds in solution[137]. It was found that an increase in temperature lowers the fractional number of radicals which recombine in the solvent cage. For azoethane in iso-octane solution this fraction (f) is 0.852 at −80 °C, 0.670 at 0 °C, and 0.539 at +85 °C. The quantity $F = f/(1 - f)$ corresponds to the ratio of the probabilities of the radicals recombining in the cage or emerging from it. In Arrhenius ($\lg F$, $1/T$) coordinates a straight line is obtained, giving an effective activation energy $E_a = E_{cage} - E_{diff}$ which is independent of the nature of the solvent and varies from −5.5 to −11.8 kJ mole^{-1} for different azo compounds.

The presence of parallel reactions can also account for the decreased rate of sulphochlorination of paraffins by the scheme $RH + SO_2 + Cl_2 \rightarrow RSO_2Cl + HCl$ when the temperature is raised, as a result of the increased rate of the direct chlorination $RH + Cl_2 \rightarrow RCl + HCl$.[138] An increase in temperature also lowers the rate of liquid-phase sulpho-oxidation of paraffins[139]. In this case the mechanism is similar to the development of a NTC in the gas-phase oxidation of hydrocarbons. The main product, the sulphonic acid RSO_3H, is formed by the gradual accumulation of persulphonic acid in the chain reaction

$$R^{\cdot} + SO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RSO_2^{\cdot} \xrightarrow{O_2} RSO_2O_2^{\cdot} \xrightarrow{RH} RSO_2O_2H\ ,$$

followed by degenerate branching by the scheme $RSO_2O_2H \rightarrow RSO_3^{\cdot} + OH^{\cdot}$, $RSO_3^{\cdot} + RH \rightarrow RSO_3H + R^{\cdot}$. On raising the temperature we make the formation of the $RSO_2^{\cdot}$ radical less probable: this lowers the equilibrium concentration of persulphonic acid and favours side reactions. For $R = CH_3$ the ratio of the constants k_1/k_{-1} is 200 at 25 °C, 40 at 65 °C, and 1 at 150 °C.[140]

Another example of NTC in a liquid-phase chain reaction is the oxidation of β-ionone by atmospheric oxygen[141]: for a constant rate of initiation the chain length and the reaction rate decrease with increase of temperature. In this case the NTC phenomenon is associated with a change in the chain breaking mechanism, quadratic chain breaking being replaced by linear chain breaking as the temperature is raised.

A decrease in the reaction rate with increase of temperature has been observed also in the iodination of silver films[142], the bromination of 2-chloro-3-t-butyl- and 3-carbomethoxyphenanthrene in CCl_4 solution[143], the oxidation of alkaline-earth metal vapours in NO_2, Cl_2, and Br_2 atmospheres at high temperatures[144], and in the reactions of solvated electrons in irradiated melts of alkali metal halides[145].

IV. NEGATIVE TEMPERATURE COEFFICIENT DUE TO THE EFFECT OF THE MEDIUM

So far we have examined reactions in which the NTC phenomenon arises from the properties of the reacting system. In many cases a NTC may be induced by "external" causes, independent of the mechanism of the reaction. We shall discuss some cases of the development of a NTC under the stimulus of external conditions.

1. Volume Expansion of the Solvent

Reactions in solution usually take place at constant pressure, and the volume of the solution and the concentration of the reactants can vary with temperature. The thermal volume change of liquids is determined by the coefficient of volume expansion[146]

$$\alpha_t' = (1/V)(dV/dt)\ (K^{-1}), \tag{14}$$

where V is the volume and t is the temperature (°C). Putting $V = V_0$ for $t = t_0$ and changing to absolute temperatures we obtain, after integration of Eqn.(14),

$$V = V_0 \exp[\alpha_t'(T - T_0)]\ . \tag{15}$$

The contribution (E') to the observed activation energy due to the volume expansion of the solution if the corresponding changes in the concentration of reactants are not allowed for in the kinetic measurements can be calculated. If the rate of the reaction is described by the equation $w = k[A]^n$ the contribution E' due only to the change in [A] caused by the change in volume (i.e. for k = const) is given by the expression

$$E' = RT^2(d\ln w/dT) = RT^2 n(d\ln[A]/dT). \tag{16}$$

If m is the number of moles of A, $[A] = m/V$, and according to Eqn.(15) we have $[A] = m/V_0 \exp[\alpha_t'(T - T_0)$. Inserting this expression into (16) gives

$$E' = -RT^2 n\alpha_t'\ . \tag{17}$$

For a third-order reaction ($n = 3$) we obtain $E' = 2.14 \times 10^3 \alpha_t'$ kJ mole^{-1} at 293 K. Using tabulated data[146] for α_t' we

arrive at the following values of E' for typical solvents by formulae (17):

Solvent	H_2O	$(CH_3)_2CO$	C_6H_6	CH_3OH	$CHCl_3$	$(C_2H_5)_2O$	Petroleum ether
$10^3\alpha_t'$ (K^{-1})	0.21	1.49	1.24	1.26	1.27	1.66	2.25
E', kJ $mole^{-1}$	−0.45	−3.20	−2.66	−2.70	−2.72	−3.55	−4.85

Thus even in solvent with a large value of α_t' the contribution of E' to the observed activation energy is small (within experimental error limits). A negative temperature coefficient could be observed only in reactions with a very small or zero "true" activation energy, but these reactions are diffusion-limited in solutions.

2. Changes in the Physicochemical Characteristics of the Solvent

In reactions involving ions or molecules with a dipole moment the rate is very dependent on parameters such as the dielectric constant of the medium, the ionic strength of the solution, the pH, etc. The contribution to the experimental activation energy from terms arising from the temperature dependence of the properties of the medium (i) is given by the equation[110]

$$E' = -R\sum_j \frac{\partial \ln k_{exper}}{\partial i_j} \cdot \frac{\partial i_j}{\partial (1/T)} \quad . \qquad (18)$$

If the change in the property i and the corresponding change in k_{exper} caused by the change in temperature are such that the two factors in the summation of Eqn.(18) have the same sign, a NTC can be observed if the contribution E' is greater in absolute value than the true (isoparametric) activation energy. The calculation assumes a knowledge of the temperature dependence of the properties of the medium and of the effect of these properties on the reaction rate.

Detailed studies of the dependence of the rate constant of many reactions on the dielectric constant of the medium ε have been reported. If only ε is taken as the parameter i Eqn.(18) can be re-written[147]

$$E' = -R\frac{\partial \ln k_{exper}}{\partial \varepsilon} \cdot \frac{\partial \varepsilon}{\partial (1/T)} \quad . \qquad (19)$$

If the reactants are two ions of the same sign, or two dipolar molecules whose dipole moments are smaller than that of the transition state, the rate of the reaction increases with ε, whereas ε itself usually increases with decrease of temperature. If both tendencies are well developed we can expect a NTC even in reactions with a high isodielectric energy of activation.

Since the dependence of the reaction rate on ε is usually expressed in $\ln k$, $1/\varepsilon$ coordinates in both theoretical and experimental work, and the dependence of ε on temperature is given as $\varepsilon = \varepsilon_0 \exp(-LT)$ or $L = -\partial \ln \varepsilon/\partial T$,[148] it is convenient to insert these relationships into Eqn.(19). Since

$$\frac{\partial \ln k}{\partial \varepsilon} = -\frac{1}{\varepsilon^2}\frac{\partial \ln k}{\partial (1/\varepsilon)} \text{ and } \frac{\partial \varepsilon}{\partial (1/T)} = -\varepsilon T^2 \frac{\partial \ln \varepsilon}{\partial T},$$

we obtain

$$E' = R\frac{\partial \ln k}{\partial (1/\varepsilon)} \cdot \frac{\partial \ln \varepsilon}{\partial T} \cdot \frac{T^2}{\varepsilon} = -R\frac{\partial \ln k}{\partial (1/\varepsilon)}\frac{L}{\varepsilon}T^2 \quad . \qquad (20)$$

Let us calculate possible values of E'. For ionic reactions the point-charge model gives[89]

$$\partial \ln k/\partial(1/\varepsilon) = z_A z_B e^2/r_{AB}k_B T \quad ,$$

where z_A and z_B are the charges on the ions, e is the electronic charge, and r_{AB} is the distance between the charges. If $z_A = z_B$, and $r_{AB} = 3$ Å, we find $\partial \ln k/\partial(1/\varepsilon) = 185$, which agrees in order of magnitude with the value calculated[89] for the reactions of the mono-anions of dibasic acids with OH^- ions. A similar value is obtained from the Kirkwood model for the reactions of dipolar molecules. The second factor in Eqn.(20) can be calculated from tabulated values of L, which for the majority of solvents lie in the range from 10^{-3} to 10^{-2} K^{-1}.[148] It is evident from Eqn.(20) that under otherwise identical conditions the contribution E' will be a maximum when the ratio L/ε is a maximum. This ratio for a number of solvents is tabulated below:

H_2O	CCl_4	$CHCl_3$	CH_3OH	$C_2H_4Cl_2$	$(CH_3)_2CO$	$(C_2H_5)_2O$	$n\text{-}C_6H_{14}$
0.058	0.40	0.78	0.19	0.52	0.23	1.18	0.44 .

Inserting (for a reaction in $(C_2H_5)_2O$) the values $L/\varepsilon = 1.18$ and $\partial \ln k/\partial(1/\varepsilon) = 185$ into Eqn.(20) we obtain $E' = -140$ kJ $mole^{-1}$ at 300 K.

This calculation shows that in some solvents the increase in rate on lowering the temperature caused by an increase in ε can be so large as to mask the decrease in rate due to the Arrhenius factor, and it can thus produce a NTC, whereas in aqueous solutions (where L/ε is small) a NTC is much less likely. This theoretical prediction[149] was experimentally confirmed in the oxidation of naphthoquinone derivatives by potassium periodate in aqueous-alcoholic solutions[147]. At pH 6.3 it was found that $E_a = -8.2 \pm 0.9$ kJ $mole^{-1}$, whereas the isodielectric activation energy is 80 ± 2 kJ $mole^{-1}$: this corresponds to a contribution $E' = -88$ kJ $mole^{-1}$.

A similar correction to the observed activation energy can be calculated for the change in other parameters of the medium. For example, if we identify the parameter i with the pH we can use the Brønsted relation[110] $\partial \ln k/\partial(\text{pH}) = \alpha$. Since changes in pH can cause large changes in reaction rate (in either sense) the observed activation energy may be higher of lower than the true activation energy by several tens of kJ $mole^{-1}$. The temperature dependence of the influence of the properties of the medium on the kinetics of reactions in the liquid phase is discussed in Ref.150.

3. Freezing of the Solvent

If reactants in a solvent (which can also take part in the reaction as one of the reactants) are mutually miscible in the solid as well as in the liquid phase, i.e. if they form a continuous series of solid solutions, the region of existence of the liquid phase at temperatures below the melting point of the solvent can be very small. Therefore a decrease in temperature in these systems rapidly suppresses the reaction because of the freezing of the solution. On the other hand if the reactants are not accommodated in the crystal lattice of the solidifying solvent and the system forms a simple eutectic system the region of existence of the liquid phase can extend for several tens of degrees below the melting point of the pure solvent before the freezing point of the eutectic is reached. In this case when the temperature is lowered the pure solvent freezes first and the effective local concentration of the reactant in the liquid phase increases, with a corresponding increase in reaction rate in keeping with the law of mass action. Under certain conditions this contribution may exceed the Arrhenius dependence in absolute value and give rise to a NTC.[151]

By comparing experimental data on the reaction rate in frozen solutions with calculations by the Arrhenius equation for the same temperature we find that the acceleration can be as high as several orders of magnitude. The following theoretical equation has been proposed for the rate constant:

$$k = \frac{T_0 - T}{\Delta}\exp(-E_a/RT) \quad ,$$

where T_0 is the freezing point of the solvent and Δ is its cryoscopic constant[110]. The maximum rate is found at the temperature $T_{max} = [E_a^2/4R^2 + E_aT_0/R]^{1/2} - E_a/2R$. Experimental data for many systems agree satisfactorily with these equations[110].

4. Other Mechanisms

An unusual phenomenon, consisting in a large increase in the reaction rate following the rapid cooling of a solid matrix, has recently been reported. For example, an equimolar mixture of methylcyclohexane and chlorine in which free radicals are photolytically generated reacts explosively when the frozen system is cooled further[152]. The velocity of propagation of the reaction front under these conditions is ~1 m s^{-1}. According to the authors[152], internal stresses in the sample are mainly responsible for this phenomenon. Active centres can be generated in various ways in these systems. Thus if a chlorine–butyl chloride, chlorine–methylcyclohexane, or hydrogen bromide–ethylene system frozen at 77 K is exposed to γ radiation from ^{60}Co and then slowly cooled to 4.2 K no changes are observed. However, if the system is cooled rapidly a "flash" reaction is observed, preceded by mechanical disintegration of the sample. These observations suggest that the thermal mechanism does not play a major role, and that the reaction may be propagated by a self-exciting process[153–155].

An increase in temperature can suppress many heterogeneous catalytic reactions if the heat of adsorption is greater in absolute value than the activation energy of the step leading to formation of the product[156]. In biocatalytic reactions a similar reversible retardation can be produced by the reversible denaturing of the enzyme over a limited temperature range. Under these conditions we expect a bell-shaped temperature dependence of the reaction rate, characterised by an optimum temperature for the reaction[157,158].

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In conclusion we should stress that the discovery of a negative temperature coefficient in a particular system can tell us a great deal about the mechanism of the reaction. First of all we must establish whether the NTC is caused by "external" conditions or whether it is inherent in the reaction system. In the former case the appropriate external factors can be isolated by an analysis of the experimental data, and the isoparametric kinetic characteristics of the reacting system itself can be identified. In the latter case a more detailed study of the reaction kinetics over a wide range of parameters is needed (mainly, a range of temperature). It is equally important to establish the possibility of various reversible processes in the system, and if necessary to obtain their thermodynamic characteristics by independent methods.

While this review was being written several reports of NTC in new systems and of more detailed studies of known NTC were published. For gas-phase processes the following studies should be noted: the recombination of $HO_2^{\cdot}$ radicals at low pressures[159], the reactions of $OH^{\cdot}$ and $O^{\cdot}$ at temperatures typical of the upper layers of the atmosphere[160], the reactions of allyl radicals with each other and with NO over a wide range of temperature[161], etc. The NTC phenomenon has been studied in several gas-phase radical reactions: $OH^{\cdot} + HNO_3 \rightarrow$ products[162,163], $NH_2^{\cdot} + O_2 \rightarrow NH_2O_2^{\cdot}$,[164] $OH^{\cdot} + SO_2 \rightarrow HOSO_2^{\cdot}$,[165] and $Cl^{\cdot} + ClONO_2 \rightarrow Cl_2 + NO_3^{\cdot}$;[166] in this type of process the highest NTC was reported for the reaction $OH^{\cdot} + C_3H_6 \rightarrow C_3H_6OH$, in which the bimolecular rate constant decreases 15-fold as the temperature is raised from 255 to 458 K, corresponding to the equation $k = AT^{-4.4}$.[167]

Activation energies $E_{obs} = -3.2$ and -7.1 kJ $mole^{-1}$ were obtained for trimethylethylene and tetramethylethylene respectively in studies of the addition of diphenylcarbene to olefins. The results were attributed to the formation of an intermediate complex which isomerises into the cyclopropane derivative[168].

A much larger NTC was observed for the bromination of hept-1-ene,[169] and for the chlorination[170] and bromination[171] of styrene in non-polar solvents. Thus in the bromination of heptene the temperature dependence of the reaction rate is bell-shaped, with $E_{obs} = -60$ kJ $mole^{-1}$ in the range 240 to 270 K. The negative temperature coefficient in these reactions is ascribed to the participation of molecular complexes in the dark radical generation step. The NTC phenomenon in the hydrochlorination of unsaturated compounds is discussed in a recent review[172]. Model calculations of the kinetics of reactions involving molecular complexes and showing a NTC are given in Ref.173.

The relationship between the changes in physicochemical properties of the medium and the NTC has been studied in detail for the oxidation of the phosphate esters of hydroquinone by potassium periodate in aqueous-ethanolic solutions[174]. A NTC has been observed also in the solid-phase oxidation of hydrazobenzene by a stable nitroxyl radical at 238–258 K.[175]

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Lomonosov Moscow
State University
Chemistry Faculty

Translated from *Uspekhi Khimii*, 53, 753-771 (1984) U.D.C. 546.26:548.517

Synthesis of Diamond in Its Thermodynamic Metastability Region

D.V.Fedoseev, V.P.Varnin, and B.V.Deryagin

Heterogeneous and homogeneous processes in the formation of diamond at low pressures, where diamond is a metastable modification of carbon, are discussed. Data on the kinetics of the growth of diamond from hydrocarbons under conditions which give codeposition with graphite are reported, together with data on the influence of hydrogen on this process and on the resulting fractionation of the stable carbon isotopes. Chemical and plasma-chemical methods of preparing diamond and diamond-like layers are discussed, as well as methods based on the use of atomic and ionic beams. The most recent theoretical and experimental results on the homogeneous formation of diamond in the gas phase are presented.
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I. INTRODUCTION

Before the first successful synthesis of diamond from the gas phase[1] research in this area was confined to the USSR and the USA. Most of the papers published at that time dealt with the growth of diamond on diamond seed crystals by the pyrolysis of methane. Work on the synthesis of diamond in its thermodynamic metastability region is now in progress in Poland, West Germany, Britian, Japan, and other countries. New methods of synthesis of diamond have been developed, using atomic or ionic beams, and low-temperature or high-temperature plasmas. Lastly, homogeneous nucleation of diamond directly in the gas phase has been demonstrated.

The rapid development of research on the synthesis of diamond in its metastability region was stimulated by the unique properties and great technological importance of this material. Whereas the only technical use of diamond until recently was as an abrasive, the material now has potential applications in electronics and in insulating and wear-resistant coatings. Existing methods of synthesis at low pressures can be used to prepare diamond powders and to grow diamond layers (both on diamond and on other surfaces) and diamond crystals. Work on the low-pressure synthesis of diamond is also relevant to an understanding of the origin of diamonds in nature, and to a number of problems in astrophysics.

This review deals with research on the growth of diamond, one of the family of carbon forms which includes hexagonal and rhombic graphite, cubic carbon, carbynes, diamond, and lonsdalite (though even more phases have been reported in the carbon system). The review will be concerned mainly with work published since 1975: earlier work is reviewed fully in Ref.2 and partially in Ref.3.

1. Phenomenological Survey of the Synthesis of Diamond from the Gas Phase

Metastability is not a bar to the formation of diamond (or of any other form of carbon). The process of diamond growth (or of crystal growth in general) can be divided into two main stages: the formation of seeds (or nucleation stage) and the further growth of existing, stable seeds of the new phase.

The free energy of diamond is higher than that of graphite. Therefore the equilibrium partial pressures of carbon-containing gases are higher over diamond than over graphite. The equilibrium pressure of methane over diamond at 1000 K is calculated to be double the corresponding value for graphite. Therefore, for a given partial pressure of methane, the supersaturation is always smaller over diamond than over graphite. Depending on the temperature and on the total pressure, the supersaturation difference between diamond and graphite can decrease, and thus it can influence the relative rates of nucleation of diamond and graphite. Increasing the pressure of methane decreases the supersaturation difference, thereby increasing the ratio of the nucleation rates for the metastable and the stable phase[4].

In spite of its metastability at low pressures diamond is more inert towards atomic oxygen and hydrogen than graphite. The chemical bonds in the diamond lattice show sp^3 hybridisation of the atomic orbitals, whereas in graphite the hybridisation is sp^2. Replacing two neighbours of a carbon atom in the diamond lattice by hydrogen has practically no effect on the electronic interaction between neighbouring atoms, whereas the same operation in graphite alters the nature of the electronic bonds in the whole graphite ring. The differences between the interactions of diamond and of graphite with hydrogen can be likened to the differences in hydrogenation behaviour between ethane and acetylene or between cyclohexane and benzene. The differences in kinetic activity between graphite and diamond form the basis of methods of purifying diamond.

Thus by combining two processes (deposition of carbon, which yields mainly graphite with a small amount of diamond, and gasification by atomic hydrogen, which affects mainly the graphite) we can obtain a product consisting mainly of diamond. In the deposition from atomic or ionic beams the gasification process is replaced by sputtering under the influence of atoms or ions (again, diamond is more impervious to sputtering than graphite).

Let us discuss the growth and gasification of diamond and graphite as in Ref.5, using the subscripts α and β to denote diamond and graphite respectively.

The rates of growth of diamond and graphite can be expressed approximately as

$$v_\alpha = k_\alpha c_1$$
$$v_\beta = k_\beta c_1 ,$$

where c_1 is the concentration of hydrocarbon, and k_α and k_β are the rate constants for the formation of diamond and graphite respectively.

If the surrounding medium contains atomic hydrogen at a concentration much greater than the equilibrium value for the given temperature the rates of the reverse (gasification) reactions can be expressed as

$$v_{-\alpha} = k'_{\alpha} c_2$$
$$v_{-\beta} = k'_{\beta} c_2 ,$$

where c_2 is the concentration of atomic hydrogen, and k'_{α} and k'_{β} are the rate constants of the appropriate gasification reactions. The condition for the deposition of carbon exclusively in the diamond form is

$$v_{\beta} = v_{-\beta} .$$

Hence the minimum concentration of atomic hydrogen can easily be calculated for a given pressure of hydrocarbon:

$$c_2 = \frac{k_{\beta}}{k'_{\beta}} c_1 .$$

The rate of growth of diamond is the sum of the rates of the forward and the reverse reaction:

$$v = v_{\alpha} - v_{-\alpha} .$$

Inserting the critical concentration of atomic hydrogen we find that the rate of growth of diamond not contaminated by graphite is

$$v = v_{\alpha}\left(1 - \frac{k_{\beta}}{k_{\alpha}} \cdot \frac{k'_{\alpha}}{k'_{\beta}}\right) .$$

The above calculation ignores the effect of molecular hydrogen on the crystallisation of diamond and graphite. The corrected formulae are unacceptably cumbersome, without introducing any fundamentally new considerations.

Thus the problems in the synthesis of diamond in its metastability region do not concern the formation of diamond itself: they relate to the prevention of the appearance of the stable phase (graphite), which would otherwise block the diamond nuclei.

The most specific property of carbon is its ability to form strong interatomic bonds with different types of hybridisation of the electronic orbitals, giving different crystal structures which are stable under normal conditions. The chemical potentials of these structures differ only by a small amount, and during crystallisation under high supersaturation this difference plays a negligible role. At the same time the energy barrier to be surmounted in the conversion of diamond into graphite is quite high. Therefore a carbon layer deposited by crystallisation at a high rate will (in general) contain structural fragments corresponding to sp^3, sp^2, and sp hybridisation of the atomic orbitals. This explains the difficulty in preparing perfect crystals of any allotropic modification of carbon (not only diamond).

In the growth processes at relatively high temperatures the energetically less favourable structures are partly converted into the more stable forms. Therefore the relative content of the various types of bond in carbon condensates produced at high temperatures cannot be used to characterise directly the kinetics of their formation from the gas phase.

Another important consideration concerns the two distinct aspects of the synthesis of diamond in general (not only in the metastability region). The first aspect is "purely chemical", and concerns the preparation of a carbonaceous substance in which the atoms are joined by bonds of the type found in a diamond crystal. The second aspect is crystallographic. It is not enough to prepare a carbonaceous substance with bonds of the diamond type if the aim is to produce a diamond: we must also organise the ordering of the crystal structure over regions of adequate size. The solution of this problem presents some major (and well known) difficulties even in substances with far fewer polymorphic modifications. The difficulties increase with the degree of crystalline perfection required. We consider that the main difficulty in the synthesis of diamond in its metastability region lies in identifying conditions compatible with the successful solution of both aspects of the problem.

We know that in organic chemistry the production of metastable compounds is the rule rather than the exception. In this sense the possibility of preparing a diamond-like carbon substance should not appear too remote to a chemist. Obviously, at moderately high temperatures ($\lesssim$1200 °C) the product will be obtained in the solid phase. However, unless precautions are taken to prevent the formation of graphite or carbyne carbon, one is faced with the difficult problem of isolating the diamond-like carbon in a pure form and identifying all the components of the deposited layer. The widely different properties of carbon condensates are due to differences in their content of diamond-like, carbyne-like, and graphite-like bonds.

This "mixed" state of the carbon layer is of interest because it should mirror some properties of the carbon modifications, which are determined by the nature of the interatomic bonds. For example, we know that in semiconductors the principal features of the energy spectrum are retained after transition into the amorphous state. Thus we could expect amorphous carbon to display a combination of the energy spectra of carbyne, graphite, and diamond, except for the contributions from long-range order effects. Thermodynamically such a phase must, of course, be unstable even with respect to the metastable crystalline modifications. At high temperatures solid-state reactions of the $sp^3 \rightarrow sp^2$ and $sp \rightarrow sp^2$ type are possible in the condensed layer, accompanied by annealing of the energetically less favourable types of bond, which brings the system closer to equilibrium (i.e. to the graphite phase).

It is reasonable to ask whether amorphous carbon can be produced at low pressures in a state displaying the short-range order of graphite or of diamond. Amorphous diamond is easily envisaged, by analogy with amorphous silicon and germanium, but amorphous graphite is almost impossible to conceive. Nearly all the specific properties of graphite arise from its strongly developed layer structure. The nearest atom from a neighbouring layer comes only into the fourth coordination sphere. Merely to retain the graphite properties due to the presence of hexagonal rings in the base planes of the graphite crystal requires a higher structural organisation than is usually assumed in amorphous substances (retention of the short-range order only, i.e. second coordination sphere). At best we can expect the existence of amorphous carbon with sp^2 hybridisation of the electronic orbitals of the C atoms.

Thus the problem of preparing diamond under conditions of thermodynamic metastability is found (on closer inspection) to be wider than expected. It should be formulated as a problem in the crystallisation of carbon at relatively low temperatures. We should stress that diamond is a classical three-dimensional ordered structure with a high degree of symmetry. A graphite crystal consists of two-dimensionally ordered networks. Carbyne is classified as a linearly ordered chain structure. Diamond, graphite, and carbyne can themselves exist in several modifications.

II. GROWTH KINETICS OF DIAMOND POWDERS

1. Co-crystallisation of Diamond and Graphite

The kinetics of diamond growth in the pyrolysis of hydrocarbons have been studied mainly during growth on diamond seed powders[6-8], using a gravimetric method (MacBain balance) to

determine the rate of deposition of carbon from the gas phase. The growth of diamond on the diamond seed powder is accompanied by deposition of graphite, which blocks the surfaces on which diamond can form. The rate of growth of graphite from hydrocarbons is lower than the rate of growth of diamond, and therefore the overall rate of deposition of carbon (by weight) decreases with time. From the initial linear portion of the plot of weight against time we can identify the growth rate of the diamond.

Most of the experiments (in different laboratories) were carried out with methane. It was shown that the growth of diamond is proportional to the partial pressure of methane over a wide range of pressure[2], i.e. the reaction is described by a first-order equation. At pressures of 0.01–0.5 mmHg and 1100–1300 K the activation energy of the diamond growth reaction was found[6] to be 80 kcal mole^{-1}.

The kinetic equation for the growth of diamond is

$$v_\alpha,\ \text{g cm}^{-2}\,\text{s}^{-1} = 3.5\cdot 10^{11}\cdot c_0 \exp(-80\,000/RT),$$

where c_0 is the concentration of methane (g cm^{-3}).

The growth rate of diamond and its activation energy are sensitive to the experimental details of the deposition process, the previous history of the sample, and the form of the diamond powder used as a seed. A gravimetric method was used also by Chauhan and co-workers[7], who heated the scale pan containing the diamond seed powder by radiation. In this way the methane not in contact with the diamond seed was kept cool. Pressures up to 44 mmHg were used. The rate of growth of diamond was found to be proportional to the pressure of methane, and an activation energy of 55 kcal mole^{-1} was obtained. Tesner and co-workers[8] studied the growth of diamond at pressures up to 3 atm and observed a slight change in growth rate above 0.5 atm, possibly due to the accumulation of hydrogen in the grown layers of the powder.

Defects on the surface of the diamond powder have a large effect on the rate of growth of diamond. Irradiated diamond powders have been used[9] in a study of the growth of diamond by the gravimetric method and by electrical conductivity measurements. Changes in electrical conductivity are due to the formation of a conducting layer of graphite on the surface of the particles. Diamond powders of ASM-10/7 grade (synthetic diamond powder of 7–10 μm particle size) were irradiated at room temperature by an electron beam of 1 MeV energy to a total dose of 3.6×10^{22} eV cm^{-2} or by γ rays from a cobalt source to a dose of 4.8×10^9 rad. Growth took place from a 1 : 2 mixture of methane and hydrogen at a total pressure of 0.35 mmHg and temperatures of 950 and 1000 °C. The sample was heated to the experimental temperature and cooled back to room temperature in a stream of hydrogen. The aggregate quantites of deposited diamond and graphite were measured by the increase in weight, and the relative amount of graphite by the conductance of the layer.

These experiments showed that the electrical conductivity after the growth is higher, and the increase in weight is lower, for irradiated diamond powders than for powders used without previous irradiation. This suggests a strong deposition of graphite on the irradiated powder, evidently due to an increase in the rate of nucleation of graphite in the presence of surface defects. The dependence of the conductivity on the growth time shows that irradiation of the powder increases the rate of formation of non-diamond carbon but does not cause marked graphitisation of the existing surface. Thus the imperfections in the diamond crystal lattice weaken the orienting effect of the surface forces leading to auto-epitaxial growth of the diamond crystal, and favour the formation of the stable carbon phase (graphite).

Methods used to free the grown diamond powder from graphite include gasification in hydrogen at 50 atm and 1000 °C, oxidation by atmospheric oxygen[2], and gasification by atomic hydrogen generated by a hot tungsten wire[10]. In a recently developed method the graphite is removed in the plasma of a glow discharge in air. The method relies on the difference between the activities of diamond and of graphite towards reactions with oxygen atoms and ions[11–13]. At low temperatures the difference between the specific rates of oxidation of diamond and graphite is five orders of magnitude. On raising the temperature the rate of oxidation of diamond in the air plasma is found to increase much faster than the rate of oxidation of graphite. The activation energy for the interaction of diamond with the air plasma is 46 kJ mole^{-1}, whereas that of graphite is 5.0 kJ mole^{-1}. At temperatures above 500 °C the activation energy for diamond increases because the interaction with molecular oxygen becomes appreciable. The nitrogen in the air plasma was shown (in separate experiments) to be almost inert at temperatures up to 800 °C.[11]

Exposure of the grown diamond powder to the air plasma completely removes the graphite from the surface, leaving a layer of grown diamond. The effective depth of penetration of the gasification reaction is determined mainly by the loss of active particles in the layer of already purified diamond. Similar results were obtained for the gasification of diamond and graphite in the plasma of a glow discharge in hydrogen[14]. This work has shown that atomic oxygen and atomic hydrogen are the main components of the gas mixture during its reaction with graphite.

Three growth rates can be defined in studies of the growth of diamond powders: $v_{\alpha\alpha}$ (the rate of growth of diamond on diamond), $v_{\beta\alpha}$ (the rate of growth of graphite on diamond), and $v_{\beta\beta}$ (the rate of growth of graphite on graphite). A suggested method[15] of determining these three rates is based on Kolmogorov's theory of the growth and merging of planar nuclei. According to the experimental results[15], at a methane pressure of 0.3–10.0 mmHg, 1 : 1 dilution with hydrogen, and 930 °C temperature the rates $v_{\alpha\alpha}$, $v_{\beta\alpha}$, and $v_{\beta\beta}$ are approximately in the ratio of 7 : 2 : 1. The quantity of diamond formed during the growth was determined[15] by gasification in a glow-discharge plasma.

Defect "healing" processes, and annealing of internal stresses, can take place during growth on diamond powders. A study[16] of the effect of over-growing in methane at temperatures up to 1600 °C on the crushing strength of diamond powders has shown that the thermal stability of the grown powder is increased by the treatment.

2. Mechanism of the Growth of Diamond on Seed Crystals

The kinetics of heterogeneous chemical reactions with formation of a new phase depend on the reactivity of the gas molecules and on the nature of the surface. The effect of the surface is two-fold. Firstly, the surface influences the kinetics of formation of the new phase through its molecular and valence forces. Formally this effect consists in a change in the energy of formation of the critical nucleus of the new phase (i.e. the nucleus capable of further growth). Secondly, the nature of the surface determines the collision frequency in the two-dimensional adsorption layer, and the frequency of encounters of "incident" molecules and atoms with sub-critical nuclei. This effect of the surface is expressed through the adsorption characteristics of the surface–gas system.

The diamond growth mechanism described below applies to systems without a super-equilibrium concentration of atomic hydrogen, in which the supersaturation is due exclusively

to a super-equilibrium concentration of methane. By analysing experimental results it was shown[17] that the rate of growth of diamond is the sum of two terms:

$$v_\alpha = k_{\alpha 1}(1-\theta_1-\theta_2)p_1 + k_{\alpha 2}\theta_2 p_1 \ , \qquad (1)$$

where θ_1 and θ_2 are the fractions of the surface occupied by methane and by hydrogen respectively, p_1 is the partial presssure of methane, $k_{\alpha 1}$ and $k_{\alpha 2}$ are the rate constants, b_1 and b_2 are the adsorption constants of methane and hydrogen respectively, and p_2 is the partial pressure of hydrogen. A theory of the growth of diamond was developed by using an adsorption equation of the Langmuir type in the form (for a binary mixture)

$$\theta_1 = \frac{p_1/b_1}{1+p_1/b_1+p_2/b_2}, \quad \theta_2 = \frac{p_2/b_2}{1+p_1/b_1+p_2/b_2} \ . \qquad (2)$$

The first term in the right-hand side of Eqn.(1) corresponds to the mechanism of direct addition on a part of the surface of the diamond seed crystal which is free from adsorbed molecules. The second term corresponds to the growth of diamond through the chemisorbed hydrogen.

We note that according to the physicochemical theory[18] of graphite growth the growth rate is given by the expression

$$v_\beta = k_{\beta_1}\theta_1^2 + k_{\beta_2}\theta_1 j_1 \ , \qquad (3)$$

where $k_{\beta 1}$ and $k_{\beta 2}$ are the rate constants and j is the flux of methane molecules per unit surface per unit time. Eqn.(3) satisfactorily describes the rate of growth of graphite at 800–1800 °C and methane pressures between 10^{-5} and 30 atm. The first term in Eqn.(3) describes the growth of graphite from the adsorbed two-dimensional gas, the second describes the growth by direct collisions. At low temperatures the graphite grows by the Langmuir mechanism, at high temperatures by the Rideal mechanism. Eqn.(3) was obtained by assuming that the formation of critical nuclei (nucleation step) is rate-limiting in the growth of graphite.

3. Growth of Diamond from Different Hydrocarbons and from Their Mixtures

The study of the growth of diamond from different hydrocarbons[19] is of interest for several reasons. Firstly, it had been suggested[20] that diamond can grow from the gas phase only in the presence of compounds whose decomposition produces methyl radicals. Secondly, the rate of growth of diamond in several hydrocarbons is higher than in methane. Lastly, the problem is of interest also in relation to the formation of natural diamonds outside the Earth's mantle.

In these experiments[19] the hydrocarbon pressure was varied between 10^{-2} and 1 mmHg, and helium was used as the carrier gas. Electrification effects were minimised by coating the quartz helix, the support, and the quartz pan of the MacBain balance with a thin layer of pyrolytic carbon. Diamond growth was confirmed by cleaning the seed powder in an air plasma after the growth: after removal of the non-diamond carbon the diffraction patterms of the samples showed only reflexions from the diamond lattice. Growth was at temperatures between 1000 and 1300 K. In all the hydrocarbons the rate of growth of diamond was directly proportional to the partial pressure of the hydrocarbon. Therefore the results can be described by the rate constant for a first-order reaction (g cm^{-2} $mmHg^{-1}$).

The activation energy for the growth of diamond was calculated[19] from the temperature dependence of the rate constant of the reaction. The lowest rate constant and the highest activation energy (80 kcal $mole^{-1}$) were obtained for the growth of diamond from methane, and the highest rate constant and lowest activation energy for the growth from acetylene. The straight-line kinetic plots for other hydrocarbons lie between those for methane and acetylene.

If these kinetic lines are extrapolated towards higher temperatures they all intersect at ~1400 K. This is the temperature above which diamond cannot be grown with the substrate and the gas at the same temperature[1,2,7,20] unless the gaseous medium is additionally activated (for example, by an electric discharge). At 1400 K and above only graphite grows on the diamond seed powder, completely suppressing the growth of diamond, because at these temperatures the rate constant for the growth of graphite from all the hydrocarbons becomes greater than the rate constant for the growth of diamond. We may assume that at high temperatures the orienting (auto-epitaxial) effect of the substrate on the formation of the new phase becomes weaker, allowing the carbon to crystallise in the stable form.

However, it should be possible in principle to obtain diamond at temperatures up to the spontaneous graphitisation temperature (~2000 K). An increase in temperature at constant total pressure in the system lowers the equilibrium partial pressure of methane over graphite and diamond, i.e. it increases the supersaturation. As a result the relative difference in the work of formation of the critical nucleus between diamond and graphite decreases, and the relative probability of the nucleation of diamond increases.

The growth of diamond from methane at high temperatures has been studied[21] by using laser heating. A diamond single crystal in a methane atmosphere was heated by the focussed radiation from a laser. The temperature of the crystal was measured by an optical pyrometer. After the growth the crystals were washed in boiling perchloric acid to remove graphite, and the remaining film was studied by reflection electron diffraction. The temperature range was 1300–2000 K, the pressure range of carbon-containing gases was 1–50 mmHg. The experiments with acetylene and ethylene gave only graphite layers. Growth from methane gave polycrystalline diamond films up to 3 μm thick. Structural studies showed that the films contain some highly dispersed graphite. The diamond and diamond–graphite films were prepared from methane at temperatures above 1600 K.

If the direct collision mechanism is applied to the crystallisation from a mixture of hydrocarbons, additivity of the reaction rates is always expected. The reaction rate is directly proportional to the flux of molecules to the surface of the seed crystal, which is linearly dependent on the partial pressure of the hydrocarbon (ignoring the changes in diffusion coefficient if the process is known to be activation controlled).

Additivity of the reaction rates was observed for the growth of graphite in methane–acetylene and ethane–ethylene mixtures[22,23]. However, deviations from additivity of the reaction rates were also noted[24,25] in the growth of diamond and of graphite, i.e. the growth rate of diamond and graphite from a mixture of hydrocarbons was not equal to the sum of the growth rates from the individual hydrocarbons at the same partial pressures. This is because in the growth of a new phase from adsorbed molecules the rate is proportional to the coverage of the surface, which in the case of a mixture of hydrocarbons is not (in general) equal to the sum of the coverages by the individual hydrocarbons. This interpretation is confirmed by experiments on the synthesis of diamond from methane–acetylene and ethane–ethylene mixtures[25] in which the growth rate of diamond from the mixtures was shown to be lower than the sum of the rates of growth from the separate gases. The apparent activation energy was a function of the composition of the mixture.

4. Effect of Added Hydrogen on the Growth of Diamond

The addition of hydrogen affects the growth of diamond from hydrocarbons in several ways. Firstly, the addition of hydrogen to the initial hydrocarbon lowers its rate of decomposition, and therefore also the rate of formation of the solid phase. Secondly, the dissociation of molecular hydrogen produces atomic hydrogen, which can gasify the graphite formed in the reaction. In the presence of a super-equilibrium concentration of atomic hydrogen the formation of graphite can be completely suppressed. According to the proposed mechanism, the rate of growth of diamond can be increased by diluting the hydrocarbon with hydrogen[26]. At temperatures above 1050 °C the rate of growth of diamond from methane–hydrogen mixtures is higher than from pure methane. Similar effects were found in ethane and propane. We can assume that the decrease in the growth rate of diamond from pure hydrocarbons caused by an increase in temperature is due to the preferential deposition of carbon in the graphite form. Dilution with hydrogen suppresses the formation of graphite by lowering the coverage of the surface with methane or methyl radicals. Under these conditions the rate of growth of graphite (on a graphite surface) is strongly lowered.

Experiments on diamond growth on an ASM-10/7 powder from methane–hydrogen mixtures and from pure methane at 1000 °C have been reported[26]. Growth was stopped at a prescribed value of the electrical conductivity of the powder, i.e. for a constant amount of graphite in the product. The weight of powder in all the experiments was the same (400 mg). We note from the results (Table 1) that for a fixed amount of deposited graphite the increase in weight of the diamond powder is greater when the methane is diluted with hydrogen than in the pure methane. On increasing the pressure the influence of added hydrogen on the growth rate of diamond is found to decrease.

Increase in mass (Δm) of the new phase during growth on a diamond powder from methane and its mixtures with hydrogen[26] (τ is the duration of the experiment, $\varkappa$ is the conductivity).

p_{CH_4}, mmHg	p_{H_2} mmHg	Δm, mg	τ, min	$10^{-3}\varkappa$, arbitrary units
0.03	0	0.12	45	
0.03	0.27	0.72	153	
0.30	0	0.80	60	170
0.30	0.30	1.15	120	170

The growth rate of diamond from hexane and from cyclohexane, and from their mixtures with hydrogen, has been found[19] to be independent of the degree of dilution (up to a ratio of 1 : 19) for a partial pressure of the hydrocarbon of 0.03 mmHg. In general the effect of dilution with hydrogen on the growth of diamond and graphite depends on the total and on the partial pressures, and on the temperature of the synthesis. However, dilution with hydrogen always lowers the rate of growth of graphite more markedly than that of diamond, owing to the difference in growth mechanism between the stable and the metastable carbon phase.

5. Fractionation of the Stable Carbon Isotopes

The forms of carbon found in nature as minerals contain a well defined ratio of the stable isotopes ^{12}C and ^{13}C. Without bringing the geochemical side of the problem into the discussion we can nevertheless note that diamonds are "heavier" than natural graphite in isotopic composition, i.e. they contain a greater proportion of the heavier ^{13}C isotope. Furthermore, in the kimberlite pipes the diamonds are isotopically "heavier" than the carbonates in the surrounding minerals. A study[27] of the fractionation of the carbon isotopes during the growth of diamond and graphite from methane has confirmed that the grown diamond is enriched in the heavier ^{13}C isotope whereas the graphite is enriched in the ^{12}C isotope.

The thermodynamic isotope effect is probably irrelevant here, since at 1000 °C (the temperature of the synthesis) its separation coefficient[28] is only 1.002 whereas the experimental value[27] is 1.025. The extent of separation of the stable carbon isotopes is strongly influenced by the rate of crystallisation. At very low or very high rates of crystallisation no separation is observed. The separation can be interpreted in terms of the mechanism of growth of diamond and graphite. The diamond surface is covered with a layer of chemisorbed hydrogen. Therefore one of the steps in the addition of a carbon atom to the diamond lattice is the formation of a $CH_4 \cdot H$ complex, whereas the growth of graphite involves mainly methyl radicals (as has been shown by extensive work[7]).

The separation coefficient can be equated (approximately) to the ratio of the reaction rates for the two isotopic forms[28]:

$$\alpha = \frac{k_1}{k_2} = \frac{s_1 s_2^{\neq}}{s_1^{\neq} s_2} \left(\frac{\mu_2}{\mu_1}\right)^{1/2},$$

where k_1 and k_2 are the rate constants of the reactions for the two isotopic forms, s_1 and s_2, $s_1^{\neq}$ and $s_2^{\neq}$ are the symmetry numbers for the isotopic forms of the compounds and of the transition complexes, and μ_1 and μ_2 are the reduced masses of the isotopic forms. Calculations by the above formula give $\alpha(CH_4 \cdot H) \approx 1.025$ and $\alpha(CH_3) \approx 0.975$, in good agreement with the largest experimentally observed[27] separation coefficients of the stable carbon isotopes.

The discussion so far has dealt exclusively with diamond and graphite. However, many other phases are present in the carbon system[29], and could be formed during the pyrolysis of hydrocarbons. Cubic carbon and alpha-carbyne have been observed[30] during the growth of diamond on powders from methane.

III. PREPARATION OF DIAMOND LAYERS AND CRYSTALS

1. Chemical and Plasma-chemical Methods of Preparing Diamond Layers and Crystals

As was shown above, the main problem in the synthesis of diamond is not organising the formation of the diamond solid phase but preventing the deposition of carbon in its stable form (graphite). Therefore all the studies of the growth of large and thick diamond films are essentially developments of methods for removing graphite and preventing its formation.

In the chemical methods this is achieved by gasifying the graphite with atomic hydrogen and with the radicals formed by activating the gaseous medium. In the first successful method of growing diamond single crystals (the pulse method[1]) the graphite nuclei formed on the surface of the seed crystals

were "re-absorbed" (gasified) in the periods between two pulses, when their diameter was still subcritical. The method gave not only monocrystalline diamond films up to 10 μm thick but also filamentary and isometric diamond crystals.

Diamonds have been grown[31,32] in a methane–hydrogen mixture activated by a glow discharge. Excitation of the electrical discharge brings the gas mixture into a strongly non-equilibrium state, with a concentration of atomic hydrogen well above the equilibrium value for the given temperature. This atomic hydrogen can interact very actively with the graphite. If a layer of graphite is previously deposited on the surface of the diamond seed crystal it is possible to remove this layer and then begin to grow a diamond layer on the clean seed surface by this method. At first only natural diamonds in the octahedral habit were used as substrates in these experiments. It was shown that a thin film of diamond grows initially in the same orientation as the substrate. This is followed by a fully mis-oriented diamond layer, and lastly by diamond layers with a rhombododecahedral texture axis. This change in orientation suggests that at high supersaturations the effect of the substrate is not very marked. Polycrystalline diamond films were deposited on silicon, molybdenum, and rhenium by the same method.

Diamond layers on a diamond substrate (and also on tungsten and gold surfaces) have been prepared by chemical transport reactions[33,34]. The method also gave separate single crystals of diamond up to 50 μm in diameter on metallic substrates[35].

The properties of diamond films prepared by chemical reactions are identical to those of natural single crystals of diamond. Unlike the diamond films deposited from ionic and atomic beams, the chemically deposited films have a high graphitisation temperature. This is obviously due to their higher crystallinity, resulting from the higher synthesis temperatures used in the chemical methods.

In the plasma-chemical methods the plasma acts both as a source of carbon and as a source of ions, which bombard the surface of the growing crystal. The ions (for example, hydrogen) and the radicals formed in the plasma can remove non-diamond forms of carbon by chemical reaction or by sputtering. The first plasma-chemical synthesis of diamond was reported in Ref.36: a black layer of carbon, with a surprisingly high hardness, was found on the cathode when a glow discharge was struck under certain conditions in an atmosphere of gaseous hydrocarbons. A layer several μm thick was obtained from a glow discharge in acetylene. Laue diffraction patterns from separate regions of the layer, which were easily recognised, indicated a cubic structure, and the Debye diagrams clearly showed two strong diamond lines but no strong graphite lines.

The electrical conductivity and the optical absorption of films prepared by the decomposition of acetylene in a direct current glow discharge at 25–375 °C have been studied[37]. The electrical conductivity of the films covers a range of 11 orders of magnitude, depending on the growth temperature. The width of the energy gap, calculated from optical absorption data, lies between 0.9 and 2.1 eV and decreases as the deposition temperature is raised. The films become graphitic[37] at temperatures above ~425 °C.

Semiconducting films of hydrogenated amorphous carbon obtained by this method were doped with boron and phosphorus during their growth[38]. Diamond crystals of various shapes (polyhedra, platelets, needles) have been obtained[39] from a plasma excited in a low pressure of aliphatic hydrocarbons by a high-voltage d.c. or a.c. (10^7 Hz frequency) source.

The pulsed crystallisation of diamond and diamond-like carbon has been described[40], using either the gas and the cathode material or the cathode material alone as the source of material for the crystallisation. In either case the carbon is present as excited atoms or ions. Chemical reaction takes place during the expansion of the plasma, when the high-temperature components should condense. The crystallisation products are deposited on a substrate (monocrystalline silicon, glass, polycrystalline aluminium) at 300 K. Layers up to 1 μm thick had good adhesion and an electrical resistance of ~10^8 Ω in the transverse direction. Diamond, lonsdalite, and other phases were detected in the deposited layers. When the substrate temperature was raised to 723 K an amorphous layer giving diffuse diffraction lines was obtained. Applying a potential of ±800 V to the sample did not affect the stucture or the properties of the deposited layers.

A study[41] by X-ray photoemission spectroscopy of films prepared by a high-frequency plasma in butane showed that diamond-like material is obtained at moderate applied power and low rates of deposition. However, the authors stress[41] that these layers are not true diamond material and should be called diamond-like.

2. Deposition of Diamond Layers from Atomic and Ionic Beams. Physical Methods

Physical methods have been used increasingly in recent years; they consist in the deposition of carbon on various (usually cooled) substrates from beams of fast carbon ions or atoms. Depending on the deposition conditions we can distinguish the condensation from atomic beams from that from ionic beams, and from flows of carbon plasma. The condensation from atomic beams uses a stream of atoms produced by cathodic sputtering of graphite electrodes. In contrast to the stream of carbon vapour produced by thermal evaporation or in an arc, in this case there are no polyatomic groups to act as nuclei for the growth of graphite. According to calculations[42] the average energy of the atoms is greater than 100 eV. The most characteristic feature of deposition from an atomic beam is the low temperature of the substrate (usually the temperature of liquid nitrogen). This, together with the low growth rates (up to 10 Å min^{-1}) and the associated low energy flux (~3×10^{-3} W cm^{-2}), ensures that the deposited layer is amorphous and homogeneous. These features also explain the stringent purity requirements on the starting materials and the need for ultra-high vacuum conditions (better than 10^{-9} mmHg).

In deposition from atomic beams the energy of the condensing atoms is difficult to control. This problem disappears when ionic beams or streams of carbon plasma are used for the deposition. It has been suggested[43] that the techniques and procedures previously used to prepare crystals of the stable modifications could be used also in the preparation of carbon condensates with the diamond structure. The basic assumption in this method is that the energy needed for the nucleation and growth of a thin layer can be supplied as kinetic energy of the condensing material rather than by heating the substrate. It is thought[43] that by using ion beam techniques both amorphous and crystalline carbon films can be prepared, and the deposited layer should be crystalline whereas its surface layers are amorphous, since not all the surface atoms have enough energy to migrate instantly to a crystalline region. The mobility of the surface atoms can be increased by adding inert gas atoms (for example, argon) to the stream of carbon atoms. This scheme was subsequently adopted in practical applications and called the double beam method[44].

As was pointed out above, the general considerations concerning the organisation of the crystal structure are equally applicable to diamond, but only under conditions which ensure the suppression of the stable modification of carbon (graphite). Therefore the conditions of the irradiation of the growing surface with accelerated atoms of carbon or of an inert gas should be chosen primarily with the aim of preventing the formation of non-diamond forms of carbon.

The importance of suppressing the formation of non-diamond forms during the crystallisation of diamond from an ionic beam has been stressed in a paper[45] describing studies of the structural and other properties of condensates prepared by this method. The energy of the carbon and argon ions (when argon was used as a carrier) was ~50 eV. The structure of the resulting layers was determined by X-ray diffraction. The technique needed long exposure times and layers at least 2 μm thick. In many cases definite but weak diamond reflexions were observed. Much thinner (100 Å) films were studied by transmission high-energy electron diffraction, in selected areas containing relatively large crystals. In this way diffraction patterns for both monocrystalline and polycrystalline material were obtained. Bright-field photography shows many monocrystalline regions with a fourth-order symmetry axis extending over cross-sections of 1–5 μm. We note that the diffraction patterns include reflexions which are forbidden for diamond, corresponding to the interplanar spacings $d_{100} = 3.57$ Å and $d_{110} = 2.52$ Å. Some diffraction patterns show sharp reflexions from the (211) planes ($d_{211} = 1.44$ Å). The presence of forbidden reflexions is attributed[45] (by analogy with the diffraction patterns of natural diamonds) to the regular occurrence in the lattice of atoms of the inert gas used as a carrier, giving rise to superlattices. The preferred (111) orientation of the layers suggests that the growth rate of the crystallites is a maximum in this direction. This was ascribed to the greater stability towards graphitisation of the (111) plane in a diamond crystal.

These results have been confirmed by a study[46] of the dependence of the phase composition and structure of the deposited layers on the composition of the beam, the energy of the ions, and their density in the beam. By using a high-current mass spectrometer with magnetic mass separation of the ions it was possible to deposit layers from spectrally pure beams of ions of the required mass and 30–100 eV energy under ultra-high vacuum conditions (5×10^{-9} mmHg). Deposition on KCl crystals gave a preferential (≥80%) orientation of the crystallites in the (100) direction, corresponding to the orientation of the substrate, but a small number of samples showed a (110) orientation. In the whole energy range (30–100 eV) the diamond phase was formed at current densities between a few hundredths and a few units of mA cm^{-2}.

It has been pointed out[47] that in the crystallisation of diamond the situation is entirely different from the formation of stable crystals (for example, silicon) not only because diamond is metastable under the conditions of deposition of the phase but also because of the possibility of irreversible graphitisation of the diamond by radiation-induced defects. In an attempt[47] to prepare epitaxial layers on diamond it was shown that in growth from low-energy ion beams even slight surface imperfections can have a strong effect on the reproducibility of the results. The best results were obtained by deposition with ions of ~900 eV energy on carefully cleaned diamond plates heated to 700 °C. Layers a few μm thick prepared at rates of deposition of a few tenths of μm per hour invariably contained inclusions of low-density carbon. The formation of these inclusions during the epitaxial growth of diamond determines the upper limit of thickness to which a monocrystalline layer can be grown in practice.

A method of preparing diamond-like layers using two ion sources has been described[44,48]. In this case one ion source generates argon ions with an energy of up to 10 keV at current densities of 0.5–1 mA cm^{-2}, which sputter the carbon target, giving a growth rate of 5–10 Å min^{-1} of the carbon layer on the substrate. The layers have properties similar to those of ordinary thermally deposited layers unless they are simultaneously irradiated with argon ions from another source at energies between 0 and 2 keV and current densities between 0.2 and 5 mA cm^{-2}. The growth rate of the layer can be controlled between 5 and 10 Å min^{-1} (allowing for back-sputtering) by suitably choosing the current density and energy of the ions. Layers prepared in this way have properties very different from those of thermally deposited layers. In a variant of this method of deposition[49] the carbon source was a diamond powder evaporated by laser heating.

A method of preparing carbon coatings from a carbon plasma has been described[50–55]. A cooled metallic substrate is located in a plasma flow generated by an arc, and connected to a d.c. potential source negative with respect to the plasma, or to a high-frequency a.c. potential. The mechanical, electrophysical, and structural properties of the resulting condensates were studied by various methods.

To explain the formation of a diamond structure under these conditions it was suggested[53] that high temperatures and pressures (corresponding to the stability region of diamond in the carbon phase diagram) may be produced locally when the substrate is bombarded with high-energy ions and atoms. Metastable crystalline forms, including diamond, are formed by the removal of energy from the "hot" points as a result of the substrate cooling. A similar explanation[48] of the mechanism uses a dynamic concept of the synthesis of diamond and gives a rough estimate of the temperatures and pressures generated by the impact of the accelerated particles on the growth surface.

The dependence of the density of carbon condensates on the initial energy of the carbon ions has been studied[54]. For ion energies of ~50 eV the density of the condensate (4.1 g cm^{-3}) is higher than that of diamond. This large increase in density is attributed[55] to the presence of diamond and a new (C_8) carbon phase in the condensate for ion energies in the range 40 eV $\leq \varepsilon \leq$ 70 eV. The nature of the structure-formation processes under ion bombardment is discussed[54] by the following qualitative model of the dependence of the density of the condensate on the ion energy: at energies greater than 10 eV the ion can penetrate into the condensate to a depth of several interatomic distances, causing local rearrangements of the structure and the formation of point defects (mainly interstitials and vacancies). The accumulation of vacancies in the dense phases at $\varepsilon > 70$ eV and the consequent conversion into more open phases explain the decrease in density of the layers.

IV. HOMOGENEOUS FORMATION OF DIAMOND IN THE GAS PHASE

1. Theoretical Discussion of the Homogeneous Nucleation of Metastable Carbon Phases

The homogeneous nucleation of diamond in the gas phase and subsequent growth on the resulting seeds produces other forms of carbon as well as diamond. At high supersaturations the work of formation of the critical nucleus of the new phase becomes comparable to the quantity $kT = \Theta$ (a measure of the energy of the thermal motion of the atoms and molecules). However, the exact theory of nucleation is limited to low[56–58] or intermediate[59] supersaturations. At

high supersaturations some difficulties arise from the need to consider entities consisting of a small number of atoms or molecules. Therefore the analysis of the rates of nucleation at high supersaturations is only qualitative. It has been shown[60-62] that an increase in supersaturation increases the probability of nucleation of diamond as compared with graphite. A more detailed analysis is given in Ref.63.

The rate of homogeneous nucleation from the vapour is defined[56-58] as the number of critical nuclei formed in unit volume per unit time:

$$I = \frac{\alpha p^2}{\rho} \cdot \frac{(\sigma m)^{1/2}}{\Theta^2} \exp\left(-\frac{U}{\Theta}\right) , \quad (4)$$

where p is the vapour pressure, σ is the surface tension, ρ is the density of the condensed phase, m is the mass of the atom (or molecule), U is the work of formation of the critical nucleus, and α is the condensation coefficient. The rate of nucleation at constant pressure has a maximum at a value of Θ given by the condition $(\partial I/\partial\Theta)_p = 0$. Ignoring the dependence of the surface energy on the curvature of the surface and assuming a constant condensation coefficient we obtain

$$(\partial U/\partial\Theta)_p - U/\Theta + 2 = 0 . \quad (5)$$

The work of formation of the critical nucleus in the classical nucleation theory is

$$U = \frac{16}{3} \frac{\pi\sigma^3 v^2}{\Theta^2 \ln^2 (p/p_e)} , \quad (6)$$

where p_e is the pressure of the vapour in equilibrium with the condensed phase, and v is the volume occupied by each particle in the condensed state. To a first approximation we can use an expression of the type of

$$p_e = A \exp(-H/\Theta) , \quad (7)$$

where H and A are the heat of evaporation and a constant factor respectively, and have different values for the different allotropic forms. From Eqn.(6) we now obtain

$$\frac{U}{\Theta}\left[1 - \frac{^2/_3 H}{\Theta \ln p/A + H}\right] = \frac{2}{3} . \quad (8)$$

In general Eqn.(8) gives a fourth-power equation for Θ. However, because of the approximations in the analysis, the treatment has been simplified[63] by considering only the case of $p = A$, when the supersaturation is $\Theta = \infty$. This gives

$$\Theta_m = U/2 .$$

Thus different phases will have maximum rates of nucleation at different temperatures (assuming constant pressure). Each phase has a supersaturation for which its rate of nucleation is a maximum. The maximum rates of nucleation of the different phases occur at different Θ values and have different magnitudes. Increasing the surface energy lowers the maximum. The published analysis[63] is applicable to many systems as well as to the carbon system. An analysis of Eqn.(8) indicates that the probability of formation of metastable phases increases with pressure.

2. Experimental Studies of the Homogeneous Nucleation of Diamond

The homogeneous nucleation (and growth) of diamond in the gas phase has been studied by using an electrical discharge in hydrocarbon vapours[64], by explosions in carbon-containing substances[65,66], and by laser heating[62,67].

By using the energy of an explosion the synthesis of diamond is carried out (in spite of the high dynamic pressures) at a temperature higher than the equilibrium temperature of the graphite–diamond phase transition, i.e. the process takes place in the thermodynamic stability region of graphite. This method gives very small (up to 1000 Å) diamond particles, often coloured. All the diamond crystals obtained by this method are defective and stressed.

The homogeneous synthesis of diamond has been achieved under cleaner conditions by using laser heating[63]. Liquid hydrocarbons were placed in a burette with a capillary tip. The radiation of an LG-25 infrared laser was focussed on the falling drop of octane, nonane, hexane, and other hydrocarbons. By varying the drop height (from the tip of the capillary to the focus of the lens) the time of interaction of the laser beam with the drop could be varied. The diameter of the drop was determined by the bore of the capillary. The repetition frequency of the drops was controlled by the air pressure in the burette. When the drop crossed the laser beam it was violently evaporated, and radiation was absorbed by the vapour. The vapour was strongly heated, and an aerosol containing both liquid and solid particles was formed round the drop. Some of the particles were entrained by the falling drop and collected in the cell. Samples for the structural studies were taken either directly from the aerosol on suitably located substrates or from the liquid residue.

Particles up to 20 μm in diameter (usually consisting of groups of much smaller particles) were observed in the electron microscope[63]. The average size of the particles was ~0.1 μm, their shape varied from irregular to accurately spherical. Structural studies (by X-ray and electron diffraction) identified the solid particles as diamond, graphite, and carbyne. After removal of the graphite by gas etching the solid phase contained only diamond and carbyne.

The electron diffraction patterns obtained from the diamond particles suggest the presence of strong stresses and a block structure, indicated by the line broadening. Most of the spherical particles were "amorphous to electrons", though in some cases diffraction patterns from a highly distorted diamond structure, close to amorphous, were obtained. We should note that in this work[63] particles of the hypothetical forms of carbon proposed in Ref.55 were observed (for example, C_8). The exact identification of the hypothetical forms of carbon, and their place in the carbon phase diagram, are still unsolved problems. The high stresses and defect densities in diamond particles obtained by homogeneous synthesis in the gas phase are probably due to the high growth rates under these conditions. Thus in the laser method the growth time of the diamond particle is 10^{-3} s, and in the explosion method 10^{-6} s.

An important requirement for the presence of diamond among the products of the homogeneous synthesis is rapid cooling of the resulting particles[63,65]. It has also been shown[68] that rapid cooling of polycrystalline graphite from high temperatures can induce the conversion of graphite crystals into carbyne and diamond. In these experiments[68] the temperature of the graphite did not exceed 3000 K. The mechanism of the solid-phase graphite–diamond transition at atmospheric pressure is not self-evident. It may involve compression of the graphite crystallites during rapid cooling. It has been shown[69] that the bonds of the graphite lattice are broken in molten carbon. Fast cooling may "freeze" the states which exist at high temperatures.

3. Some Consequences of the Homogeneous Nucleation of Diamond

These results may help to explain the origin of the natural diamonds found in kimberlite pipes. The diamonds could have been nucleated by local explosions, with gaseous hydrocarbons as the source of carbon. Evolution of hydrocarbons

occurs (as it did at the relevant time) in practically all the pipes containing diamonds. However, calculations show[70] that the strength of the rocks is insufficient to contain the pressures corresponding to the region of thermodynamic stability of diamond.

Very interesting reports of the possible existence of very fine diamond particles in interstellar space have been published[71]. Carbon is the most probable constituent of cosmic dust, and carbon particles could be formed from matter ejected by stars. The carbon–nitrogen cycle, formulated by Bethe in 1939, is a source of thermonuclear energy in hot stars. When matter is ejected from a star and rapidly cooled the carbon vapour can condense into very small particles. At this stage various forms of solid carbon can also be formed: graphite, carbyne, diamond, and others. The nucleation of solid carbon takes place in the presence of hydrogen. We have shown[1] that hydrogen can markedly lower the growth rate of graphite, but its effect on the growth rate of diamond from hydrocarbons is much smaller. The difference in the rates of interaction with different carbon phases is even greater with atomic hydrogen. A study[14] of the interaction of atomic hydrogen generated by a glow discharge with graphite and diamond showed that up to 500 °C the gasification of diamond by atomic hydrogen is negligible, whereas the rate of gasification of graphite is substantial. This allows complete gasification by atomic hydrogen of the graphite particles formed by the condensation of carbon atoms from the plasma of stellar matter.

The diffuse luminescence of the Galaxy is said[71] to be incompatible with the hypothesis that interstellar dust consists of particles of graphite or of graphite covered with ice. It is suggested[71] that the dust probably consists of diamond particles up to 0.1 μm in diameter. The lack of direct experimental data on the homogeneous nucleation of diamond was noted with regret, and it was stated that the diamonds in the Galaxy must have a high concentration of defects (as has been found in the experiments discussed above). The phase composition of the carbon in interstellar dust could have a direct bearing on the conversion of the initially atomic hydrogen in interstellar matter almost totally into molecular hydrogen[72].

The recombination of two hydrogen atoms into a molecule requires the presence of a third particle, which could be a particle of interstellar dust. Many different organic compounds, containing hydrogen, nitrogen, oxygen, and other atoms, are found in dense interstellar clouds. When considering the evolution of such a cloud we must allow for the fact that the reactivity of graphite towards atomic hydrogen and oxygen is very high, whereas that of diamond is negligibly small. The reaction of hydrogen atoms with graphite at low pressures can produce various radicals and compounds, some of which have been observed by radio-astronomical methods in interstellar space (see Table 1 of Ref.72). Therefore the formation of organic compounds in interstellar clouds may be due (at least, partially) to the gasification of graphite particles in the interstellar dust. On the other hand the recombination of hydrogen atoms could take place on diamond particles, whose presence in interstellar space seems likely.

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Institute of Physical Chemistry of
the USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 772-801 (1984) U.D.C. 541.65 + 541.67 + 543.422 + 547.1'13

The Spectroscopy of Organic Compounds of Silicon Subgroup Elements and Hyperconjugation

A.N.Egorochkin

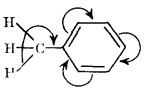
The general and theoretical aspects of the problem of hyperconjugation are examined. The factors determining the magnitude of the effect and its major role in organoelemental compounds compared with organic compounds are discussed. Various types of hyperconjugation (σ,π-, σ,σ-, and σ,p-conjugation) in the ground electronic state of organoelemental compounds of Group IV elements are considered.
The bibliography includes 226 references.

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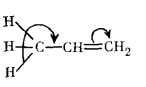
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I. INTRODUCTION

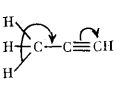
The concept of hyperconjugation was introduced into organic chemistry in connection with the study of the reactivity of aromatic compounds, the influence of alkyl substituents of which cannot be described solely in terms of the inductive effect[1,2]. By analogy with π,π- and p,π-conjugation (the interaction of π or p electrons with the π-electron system), the σ,π-conjugation (hyperconjugation) of the σ electrons of the C–H bonds π-electron systems in the ground electronic state can be represented schematically as follows[3,4]:



(I)



(II)



(III)

In the system of Hammett–Taft equations the possibility of σ,π-conjugation is attributed to the presence in the alkyl group of a considerable resonance component having the same sign as the positive inductive effect. For example, the inductive (σ_I) and resonance (σ_R) constants for the CH_3 group are respectively -0.05 and -0.12.[3] For transition states in which a positive charge arises at the reaction centre (aromatic ring, multiple bond, or a substituent linked to them in the *para*-position relative to the alkyl group), the electron-donating properties of the alkyl groups are enhanced when the hyperconjugation effect is intensified[3,4].

The enhancement of the electron-donating properties as a consequence of the positive charge is reflected in the transition from the Hammett σ_n constants ($\sigma_n \approx \sigma_I + \sigma_R$) to the Brown-Okamoto σ_n^+ constants (see, for example, Exner[5]). For the CH_3, CH_3CH_2, $(CH_3)_2$, and $(CH_3)_3C$ groups, the constants σ_n and σ_n^+ (given in brackets) are respectively -0.17 (-0.31), -0.15 (-0.29), -0.15 (-0.28), and -0.20 (-0.26).[5]

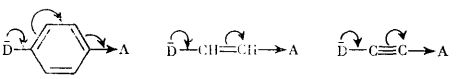
Thus the influence of alkyl groups can be twofold. The first case refers to the ground state and to transition states in which there is no direct resonance interaction between the alkyl substituent and the charged reaction centre. The influence of the substituents is then described by the Hammett σ_n constants, which vary irregularly on successive transition from CH_3 to $(CH_3)_3C$, reflecting the joint influence of the inductive effect and hyperconjugation. In this situation it is difficult to obtain information about hyperconjugation and there is a widely held view that this effect is absent in the ground state[3,6-8].

The second case refers to a transition state with a strong resonance interaction between the alkyl substituent and the positively charged reaction centre. Here the influence of the substituent is described by the σ_n^+ constants, which diminish in absolute magnitude on passing from CH_3 to $(CH_3)_3C$, i.e. vary in direct opposition to the inductive effects of these groups. This situation obtains in experiments where the concept of hyperconjugation has been resorted to in order to account for the results (see, for example, Refs.1,4, and 7–9).

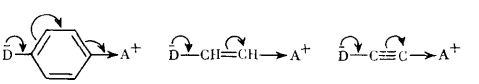
The smallness of the σ,π-conjugation effect in organic compounds and the difficulty of isolating it from the set of other factors influencing the reactivity have led some investigators to doubt the reality of this effect[3,8]. At the same time there are also many arguments in support of the existence of hyperconjugation in organic compounds[4,6,9]. As regards hyperconjugation in organic compounds with participation of C–C σ-bonds, the data on this question are extremely contradictory.

Summarising the data examined[1-4,6,8,9], taking into account the work of Kreevoy and Taft[10,11], one can conclude, following Palm[7], that hyperconjugation is one of a variety of direct polar conjugation. This conclusion is extremely significant for the understanding of the characteristic features and the major role of hyperconjugation in organoelemental compounds.

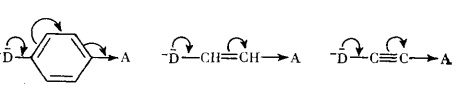
The common features of the direct polar conjugation effects in organic compounds are known (see, for example, Johnson[12] and Minkin et al.[13]). The direct polar or "through" conjugation is a resonance interaction between the *para*-substituents of the donor (D) and acceptor (A) type in the ground state (or between the *para*-substituent and the charged reaction centre in the transition state) via the π-electron system:



(IV) (V) (VI)



(VII) (VIII) (IX)



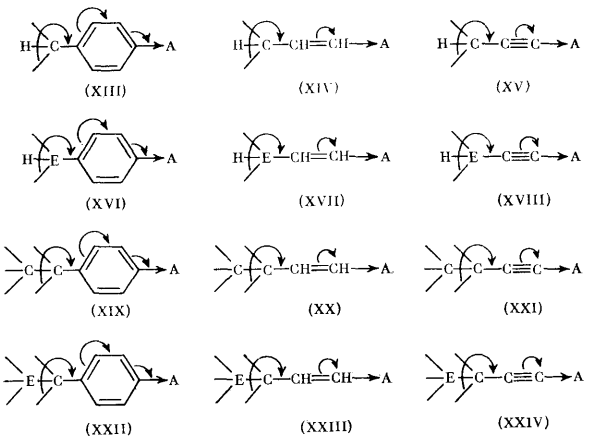
(X) (XI) (XII)

The magnitude of the "through" conjugation effect depends on the relative contributions of the donor–acceptor properties of the substituents D and A, increasing with enhancement of the electron-donating properties of D and the electron-accepting properties of A. The generation of a positive charge on A or a negative charge on D in the transition state [transition from compound (IV) to compounds (VII) and (X), from compound (V) to compounds (VIII) and (XI), and from compound (VI) to compounds (IX) and (XII)] enhances the effect considered.

When the substituent A(D) is kept constant and D(A) is varied, the magnitude of the direct polar conjugation effect varies linearly with the constants σ_R^+ of electron-donating substituents (or σ_R^- of electron-accepting substituents)[12,13].

It is also important that the polarisability of the π-electron system through which the D and A fragments interact is significant for polar conjugation[13,14]. These factors, characterising the direct polar conjugation and hence also hyperconjugation (σ,π-conjugation), which is a variety of the latter, should be especially important for organoelemental compounds for the following reasons. The electronegativities of all the central elements in organoelemental compounds are lower than the electronegativity of carbon[15]. Therefore fragments of the type EH_3 (where E are Group IV elements—silicon, germanium, tin, and lead) and EH_3CH_2, which are isostructural with respect to the methyl (CH_3) and ethyl (CH_3CH_2) groups respectively, should have more pronounced electron-donating properties than their carbon analogues as a result of the inductive mechanism. This has been frequently confirmed experimentally[5,16]. As regards the hyperconjugation mechanism, organoelemental fragments also manifest more pronounced electron-donating properties than the isostructural carbon groups[17–19].

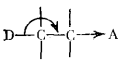
This is associated with the influence of a number of factors which are considered below, mainly with the greater polarisability of the bonds in the organoelemental compounds. By virtue of the higher polarisability of organoelemental fragments compared with the analogous carbon fragments, the effectiveness of the involvement of these fragments in the overall direct polar conjugation system is also improved. Thus the influence of the inductive effect and of the polarisability leads to an enhancement of the electron-donating properties of the substituents D in schemes (IV)–(XII), i.e. to an enhancement of the hyperconjugation in organoelemental compounds compared with their carbon analogues.



In view of the factors considered above, the influence of hyperconjugation should increase on passing from carbon compounds of types (XIII), (XIV), and (XV) to the corresponding organoelemental analogues (XVI), (XVII), and (XVIII) and also on passing from compounds (XIX), (XX), and (XXI) to compounds (XXII), (XXIII), and (XXIV).

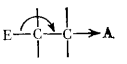
We may note that the effect of the $(p-d)\pi$ interaction between the electrons of the multiple bonds and the vacant *nd* orbitals of the E atoms is observed, together with hyperconjugation, in compounds (XVI)–(XVIII) containing the element E linked directly to a π-donor centre[20]. These effects operate in opposite directions, the $(p-d)\pi$ interaction exerting a dominant influence, as will become apparent below.

The idea of the greater role of hyperconjugation in organoelemental compounds compared with organic compounds was put forward for the first time and justified by Nesmeyanov[21] in a study of the characteristic features of the reactivities of organometallic compounds. A profound analogy is observed between the reactivities of classical test systems of the π,π- and *p*,π-types and σ,π- and σ,σ-conjugated systems (the concept of such systems was introduced by Nesmeyanov[21]). The idea of second-order hyperconjugation (σ,σ-conjugation) is indissolubly linked with the high polarity and polarisability of organoelemental compounds. The effect of the σ,σ-conjugation, expressed by scheme (XXV)



(XXV)

therefore plays a notable role only when there is a significant difference between the electronegativity of the D (donor) and A (acceptor) atoms and when the polarisability of the D–C bond is high; this can be ensured sufficiently only for organometallic compounds [as in a scheme of type (XXVI)]:



(XXVI)

where E is a silicon subgroup element or some other central atom of the organometallic compound.

The ideas concerning the effects of σ,π- and σ,σ-conjugation were initially developed in order to elucidate the characteristics of the reactivity of organoelemental compounds—its specific features compared with the properties of organic compounds. The results obtained refer to a transition state. Subsequent investigations of the effect by molecular spectroscopic and quantum-chemical methods confirmed the reality and importance of hyperconjugation in the ground and excited electronic states of organoelemental compounds and also the dependence of such conjugation on the electronic state of the molecule. In these studies the first steps were taken towards the investigation of the role of hyperconjugation on passing from a non-reacting to a reacting molecule, which is also significant for theoretical organoelemental chemistry. As a consequence of the low magnitude of hyperconjugation effects compared with other resonance effects and the complexity of the intramolecular interactions in organoelemental compounds, the experimental data for hyperconjugation are not reliable in all cases and their interpretation is not always unambiguous. Furthermore, data for hyperconjugation in organoelemental compounds are fragmentary and systematic studies in this field are only just beginning.

The main task of the present review is therefore a critical examination of data for hyperconjugation in organic compounds of mercury (as model and thoroughly investigated systems) and silicon subgroup elements, obtained by molecular spectroscopic and quantum-chemical methods.

It seems useful to characterise in a general form the criteria employed in theoretical and experimental studies in order to establish the existence of hyperconjugation and to

estimate the magnitude of the given effect. As stated above, the absence of fundamental differences between the classical conjugation effect and hyperconjugation was emphasised in the studies by Mulliken[2] and Nesmeyanov[21]; the hyperconjugation effect is merely smaller, but, on passing from organic to organoelemental compounds, the hyperconjugation becomes abruptly much more pronounced[21]. The influence of the organoelemental fragments of the molecules involved in hyperconjugation is comparable to the effect of the strongest organic donors, as will be demonstrated in detail below. Therefore the study of hyperconjugation, as a task for physical organic chemistry, consists primarily in the separation of the effects of substituents into the inductive and resonance components and, if the latter component consists of several contributions, in isolating the contribution associated with hyperconjugation. In relation to specific molecular spectroscopic methods, the solution of this problem presupposes the selection of spectroscopic parameters sensitive to the influence of electronic effects (especially conjugation effects), the correct isolation of the contributions due to hyperconjugation, and the determination of the relation between these contributions and the characteristics of the structure of the compounds studied.

As a task for quantum chemistry, the study of hyperconjugation does not reduce solely to the selection of the correct methods of study and the demonstration of the existence of this type of conjugation but consists mainly in a more profound consideration of the results of experimental studies. It is shown below that the experimental characteristics of hyperconjugation, such as the dependence on the donor–acceptor properties of the conjugated bonds and on the sign of the charge on the π-electron system, the nature of the central element in the organoelemental compounds, and stereoelectronic factors, have been justified theoretically in the quantum-chemical analysis of the total energy, the bond orders, the geometrical characteristics, and the conformations of the molecules.

II. THEORETICAL IDEAS ABOUT HYPERCONJUGATION

The work of Eaborn[22], Traylor and co-workers[23], Bock[24], and Pitt[25], which demonstrated experimentally the important role of σ,π-conjugation in systems with a positive charge in the highest occupied molecular orbital (HOMO) of the π-type in benzene derivatives, was a development of Nesmeyanov's classical ideas and stimulated a series of theoretical studies of the effect of hyperconjugation in derivatives of carbon and organometallic compounds by both non-empirical (*ab initio*) and semiempirical (different versions of the zero differential overlap procedures—CNDO and INDO) quantum-chemical methods. Strong resonance interaction between a substituted cyclopropane ring and groups of the type CH_3, $CH_2^{\cdot}$, and CH_2^+ bound to it was demonstrated by the INDO and CNDO/2 methods. For CH_2^+, such interaction is the strongest[26] and hyperconjugation is apparently partly responsible for it, although the separation of the contributions to the given interaction by the σ- and π-components is difficult[26]. (The questions concerning the electronic effects, including hyperconjugation, have been considered in relation to unsaturated cyclic compounds[27].) The possibility of resonance interactions of the type of hyperconjugation (intermediate in magnitude between the effects of saturated and unsaturated substituents) between the cyclopropane (or cyclobutane) ring and a double bond has been indicated by *ab initio* calculations[28]. The conformations and stabilities of the substituted ethyl, propyl, and butyl cations have been investigated by the same method[29].

Substituents stabilise cations to a greater extent compared with the corresponding hydrocarbons[29] and radicals[30]. The stabilising capacity of the substituent depends on the hyperconjugation and the inductive effect. The effect of hyperconjugation, which determines the preferred conformation of the cations, depends on the capacity of the bonds at a β-carbon atom for such conjugation. According to the results of Radom et al.,[29] the C–C bond has a capacity for hyperconjugation just as great as the C–H bond. The same conclusion was reached in a study of norbornylbenzenes, in which the C–C bonds involved in hyperconjugation have a marked *p* character[31]. The existence of preferred conformations of the cations $XCH_2CH_2^+$ or anions $XCH_2CH_2^-$ due to hyperconjugation follows from *ab initio* calculations[32]. Hyperconjugation determines the geometries of the given ions and the degree of conjugation depends on the nature of X.[32–34]

Within the framework of the molecular orbital theory, the stabilisation of vinyl, isopropyl, and butyl carbonium ions and of protonated toluene as a result of hyperconjugation is regarded as the interaction of the σ orbitals of strained C–H or C–C bonds (having a higher energy in the ions than in in the neutral compounds) and a suitable *p* orbital of the ion. The interaction lowers the energy of the bonding molecular orbitals of the ion[35]. These conclusions[35] can be extended also to organometallic systems having high-energy σ orbitals of the E–C bonds.

The state of the problem of the interaction of the methyl group with π-electron system has been most fully considered by Libit and Hoffmann[36]. Numerous quantum-chemical data summarised by the above workers[36] indicate a slight electron transfer from the CH_3 group to the double bond and the aromatic ring and an appreciable polarisation of the π-electron system. The polarisation involves the hyperconjugation of the σ orbital of the methyl group with the π-electron system of the double bond or the aromatic ring[36]. Some aspects of hyperconjugation have already been examined[37,38]. Thus it follows from calculations on siladispiroheptane by the extended Hückel method that, together with conjugation involving the *d* orbital of silicon, there is hyperconjugation involving the electron-accepting antibonding orbitals of the Si–H bond[38].

A series of theoretical estimates of the capacity of the E–C bonds for hyperconjugation, where E is an element other than carbon or hydrogen, have been made. Thus virtually identical capacities of the C–S and C–H bonds for hyperconjugation have been demonstrated[39,40]. According to quantum-chemical and photoelectron spectroscopic data the energy of the HOMO of the π-type in benzyl halides depends on the inductive and resonance (hyperconjugation) effects. After the separation of the effects, the energies of hyperconjugation involving the C–Hal bonds have been estimated as 0.16, 0.28, 0.33 and 0.44 eV for Hal = F, Cl, Br, or I respectively (the hyperconjugation of the C–H bonds with the benzene ring amounts to 0.12 eV)[41]. Similar estimation of the hyperconjugation energy between the C–Hal and C=C bonds yielded 0.22, 0.31, 0.45 0.63 eV for Hal = F, Cl, Br, or I respectively[42].

The hyperconjugation in organomercury compounds has been investigated by the extended Hückel method[43,44]. The calculations showed that benzylmercury bromide is most stable in the electronic ground state in the conformation which ensures the interaction of the polarisable Hg–C bond with the π-electron system of the ring (the Hg–C–C angle is 90°). As a result of the σ,π-conjugation, the $BrHgCH_2$ fragment is typically electron donating in proton exchange processes[43,45]. In conformity with Nesmeyanov's work[21], it follows from the calculations of the total energies and bond orders[43] that the replacement of the bromine atom in

$BrHgCH_2C_6H_5$ by the electron-donating CH_3 group enhances the σ,π-conjugation, while its replacement by the more electron-accepting chlorine atom weakens the effect. The effect of the σ,π-conjugation is benzylmercury bromide is much stronger than in benzyl bromide[43]. The Hg–C bond in allylmercury bromide is at right angles to the nodal plane of the olefinic π-electron system[44] and the degree of σ,π-conjugation increases in the transition state compared with the ground state. The hyperconjugation weakens on passing from allylmercury bromide to the cation $^+HgCH_2CH=CH_2$,[44] since the electron accepting properties of the mercury-containing fragments $^+HgCH_2$ in the cation are apparently enhanced.

Hyperconjugation in compounds of Group IV elements has been frequently confirmed by *ab initio* calculations and by the CNDO method. Although the non-empirical calculations[46,47] for propene and vinylsilane did not provide an unambiguous answer concerning the $(p-d)\pi$ interaction in vinylsilane (like the calculations by the CNDO/2 method[48]), they indicated definitely the existence of hyperconjugation in this compound. The latter has also been confirmed by calculations using the CNDO/2 method, which agree for allyl- and vinyltrimethyl-silanes with photoelectron spectroscopic data[49,50]. The σ,π-conjugation plays a significant role in allylsilane, which has been recently demonstrated[51] also by the MINDO/3 method. In vinyltrimethylsilane the effects of the $(p-d)\pi$ interaction and hyperconjugation act in opposite directions[49]. These conclusions for silicon-containing ethylene derivatives agree with other data[52–54] and with calculations by the extended Hückel method for the compound $(CH_3)_3ECH_2CH=CH_2$,[55] in which the significant role of the σ,π-conjugation on passing from E or C to silicon subgroup elements has been demonstrated.

The increase of the multiplicity of the bond between silicon and ethynyl groups is apparently ensured both by the σ,π-conjugation of the σ orbitals of the silicon atom with the π orbitals of the C≡C fragment[46] and by the $(p-d)\pi$ interaction of the π electrons of the multiple bond with the unoccupied 3*d* orbitals of the silicon atom[56]. It is striking that both experiment and calculations show that the inductive effect of the CH_3 group predominates over hyperconjugation in methylacetylene but at the same time they also show that hyperconjugation plays a greater role in silylacetylene than the inductive effect of the SiH_3 group[57]. Calculations for phenylsilane in terms of the CNDO/2 approximation[55] demonstrated the significance of three effects—the inductive effect, the $(p-d)\pi$ interaction, and σ,π-conjugation, which has also been confirmed by calculations using the MINDO/3 method[59] for related systems—trimethylphenyl- and trimethylbenzyl-silanes. The importance of all three effects for the former compound and the appreciable role of hyperconjugation for the latter[59] and also for benzyl derivatives of germanium and tin[54] was then established. The greater role of hyperconjugation in silylanilines compared with the carbon analogues has been demonstrated in calculations using the CNDO/2 method[60]. As in the carbon compounds[29,30,32–34], hyperconjugation has a significant influence on the conformation of ions of the type $H_3ECH_2CH_2^{\pm}$ (E = Si or Ge).[61] One cannot rule out the possibility that hyperconjugation obtains also in tetramethylsilane[62].

The familiar work by Pitt[17], in which the role of σ,π-conjugation was estimated by analysis of experimental data for compounds of Group IV elements combined with an application of molecular orbital perturbation theory and of calculations by the CNDO/2 method, has been a significant development of the problem of hyperconjugation in organoelemental compounds. The author, having developed the initial concept of, for example[63] the dominant role of hyperconjugation, emphasises the importance not only of hyperconjugation but also of the inductive effect and the $(p-d)\pi$ interaction for the interpretation of the properties of organoelemental compounds. The perturbation energy δE, arising as a result of δ,π-interaction (hyperconjugation), is defined by the expression

$$\delta E = \pm \frac{a^2(\pi)a^2(\sigma)P^2}{\Delta E},$$

where $\Delta E = E(\pi) - E(\sigma)$ is the difference between the energy of the unperturbed π and σ orbitals, $a^2(\pi)$ and $a^2(\sigma)$ are the electron densities in the *p* orbitals of the bonding atoms in the HOMO of the π- and σ-systems, and *P* is the perturbation integral, including the overlap of the *p* orbitals connecting the π- and σ-systems.

For a series of isostructural compounds with a variable central element E, for example for $(CH_3)_3ECH_2C_6H_5$, the quantities $a^2(\pi)$, $E(\pi)$, and *P* remain constant, while $E(\sigma)$ and $a^2(\sigma)$ vary, the principal contribution arising from $E(\sigma)$.[19,64,65] Since ΔE diminishes from Si to Pb, the degree of σ,π-conjugation involving the E–C bonds (characterised by the perturbation energy δE) increases as E is varied in the sequence Si < Ge < Sn < Pb,[19] which also agrees with the traditional ideas and, as will be shown below, with all the experimental data. For organoelemental compounds of the type $R_3EE'R_3$ and R_3EER_2X, there is a possibility of σ,σ- and σ,*p*-conjugation effects as a result of the pseudo-π-conjugation of the formally localised σ(ER) orbitals and, in the case of σ,*p*-conjugation, also accompanied by the involvement of the orbitals of the unshared electron pair of the atom X.[17]

The effects of the σ,σ- and σ,*p*-conjugation enhance the similarity of the molecular orbital energies, the increase of the perturbation integral *P*, and the bond polarity, which increases the electron density in the *p* orbitals of the bonding atoms. Pitt's calculations[17] confirm the increased stabilisation of the cationic centres by the R_3ECH_2 groups with increase of the atomic number of E and also the possibility of the manifestation of electron-accepting properties by the H_3SiCH_2 group relative to anionic centres.

The idea of more marked electron-donating properties of the R_3ECH_2 group compared with R_3E (although on the basis of the inductive effect alone for these groups, the opposite behaviour should have been observed—see, for example, Egorochkin et al.[66]) is very common in reviews of the properties of silicon-subgroup elements (E)[20,67–70]; this is usually attributed to the character of the σ,π-conjugation between R_3ECH_2 and the π-electron system.

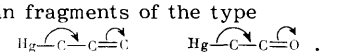
III. EXPERIMENTAL STUDIES OF HYPERCONJUGATION IN ORGANOELEMENTAL COMPOUNDS

1. Organomercury Compounds as Model Systems

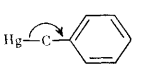
Organomercury compounds, which are widely used as model systems in organic and organoelemental chemistry, have also fulfilled this function in the study of σ,π-conjugation. These compounds were in fact the main objects of the study of the reactivity of which led Nesmeyanov and Lutsenko to the conclusion that the σ,π-conjugation plays an important role in organoelemental compounds[21,71].

In molecules containing the E–C–C=C or E–C–C=O fragments (E is a mercury or another metal atom), the σ,π-conjugation of the E–C σ-bond and the π-bond of the C=C or C=O group induces a series of specific properties. The

considerable difference between the electronegativities of mercury and carbon atoms (1.9 and 2.5 respectively) and the higher atomic number of mercury, which is in the VIth Period, are responsible for the polarity of the $Hg^{\delta+}-C^{\delta-}$ bond and its high polarisability. These factors favour the σ,π-conjugation in fragments of the type



Conjugation leads to the lability of the mercury–carbon bond and in many instances to the transfer of the reaction centre in reactions with electrophiles to the carbonyl group[71-73] and, for compounds with the fragments



to the aromatic ring[74].

The effect of σ,π-conjugation leads to the stabilisation of the transition state in the acid decomposition of allylmercury halides[44]. Hyperconjugation influences the properties of organomercury compounds not only in the transition state but also in the ground electronic state. This has been established in a series of experiments undertaken to demonstrate the very fact of the existence of σ,π-conjugation and to investigate the influence of molecular structure on the magnitude of this effect. Physicochemical experiments have confirmed the occurrence of the transfer of electron density via the conjugated system from the mercury atom to the electron-accepting molecular fragments (the multiple bond, the aromatic ring, the carbonyl group) and demonstrated the dependence of such transfer on the nature of the electron-accepting fragment and the decisive influence of the molecular geometry not only on the magnitude but also on the very possibility of the existence of the effect of σ,π-conjugation.

The data concerning the dependence of the energy of σ,π-conjugation on the molecular geometry are extremely clear. The greatest effect of σ,π-conjugation should be attained for the maximum overlap of the σ orbital of the Hg–C bond with the π orbital of the C=O (C=C, C_6H_5) group. Such overlap is ensured by the coplanar disposition of the Hg–C bond and the axis of the π orbital. When there is a marked deviation from such disposition of the interacting molecular fragments, there should be no σ,π-conjugation or it should be greatly weakened.

Experiment confirms this. Thus the closeness of the Hg–C–C angles to 90° in compounds with σ,π-conjugation was noted above[43,44]. Another characteristic example is provided by Raman spectroscopic data[75]. The intensity of the ν(C=O) bands in the Raman spectra of acyclic compounds having the Hg–C–C=O fragment and also in the spectrum of α-chloromercuricyclohexanone is appreciably higher than the intensity of the corresponding bands in the spectra of the non-conjugated ketones. On the other hand, the frequency of the ν(C=O) bands is lower in the spectra of organomercury compounds, which reflects the electron-donating properties of the mercury-containing molecular group relative to the C=O group in terms of the σ,π-conjugation mechanism and also apparently it reflects the higher polarity of the C=O bond owing to conjugation.

When the mercury-containing and carbonyl fragments are rigidly fixed in space, which rules out a resonance interaction between them, the spectroscopic characteristics of σ,π-conjugation disappear. Thus, judging from the positions and intensities of the ν(C=O) bands in the Raman spectra, α-chloromercuricamphenilone is a typical non-conjugated cyclic ketone[75].

The allyl derivatives of mercury containing the Hg–C–C=C fragment have, like the mercuriketones, Raman spectra with higher intensities of the ν(C=C) bands as a consequence of σ,π-conjugation[76,77]. However, the increase of the intensity of the ν(C=C) bands in the spectra of allyl derivatives of mercury is smaller by a factor of approximately two than the increase of the intensity of the ν(C=O) bands in mercuriketones due to σ,π-conjugation[76,77]. Thus, for unaltered electron-donating properties of the mercury-containing fragment, the intensity of the σ,π-conjugation increases with enhancement of the electron-accepting properties of the multiple bond. The latter properties are more pronounced for the C=O group (compared with the C=C group mainly owing to the greater electronegativity of the oxygen atom). The greater extent of hyperconjugation, approximately by a factor of two, in mercuriketones compared with the allyl derivatives[77] clearly illustrates Nesmeyanov's classical ideas (see Section I), according to which the hyperconjugation energy increases with the increase of the difference between the electron-accepting properties of the bonds involved in the conjugation.

Detailed study of the vibrational (infrared and Raman) spectra of organomercury compounds showed that the molecules of allyl- and benzyl-mercury halides in solutions have a non-planar configuration with the Hg–C bond located in a plane perpendicular to that of the double bond or the aromatic ring[78,79]. This constitutes yet another piece of evidence in support of the existence of σ,π-conjugation. Subsequent studies showed that a configuration favourable for σ,π-conjugation arises in the benzyl derivatives of mercury not only in solutions[33,78,80] but also in the crystalline[81] [for example, in the case of $C_6H_5CH_2HgSC(C_6H_5)_3$] and gaseous states[82] (benzylmercury chloride). The photoelectron spectroscopic data for benzylmercury chloride indicate the destabilisation of the HOMO of the π type as a result of the σ,π-conjugation and make it possible to estimate the interaction integral between the π and σ orbitals of the Hg–C type (0.99 eV). This quantity is extremely close to the value (0.98 eV) for allylmercury chloride, which, like the benzyl analogue, is a configuration necessary for σ,π-conjugation also in the gaseous phase[83].

Convincing data supporting the existence of σ,π-conjugation in organomercury compounds have been obtained by NMR spectroscopy[76,84-86]. The ^{199}Hg NMR data provide most information. The study of benzylmercury chloride and its derivatives showed that the introduction of methyl groups in the *ortho*- (but not in the *meta*- or *para*-) positions in the aromatic ring increases the fraction of conformers in which the Hg–C bond is not in the plane of the aromatic ring, favours the σ,π-conjugation, leads to an increase of the positive charge on the mercury atom (as a result of conjugation), and deshields the ^{199}Hg nucleus.

The stereochemistry of the σ,π-conjugation is also reflected in other parameters of the ^{199}Hg NMR[86] and ^{13}C NMR[76,84,86] spectra. According to chemical data, for example those of Nesmeyanov and Kritskaya[87], owing to the increase of the lability of the Hg–C bond as a consequence of σ,π-conjugation, polarographic reduction with dissociation of the bond takes place at much lower potentials for conjugated systems than for non-conjugated systems[75,76]. The electronic spectroscopic data for charge-transfer complexes (CTC) of benzyl derivatives of mercury with tetracyanoethylene are of fundamental importance[80,88]. This method makes it possible to investigate σ,π-conjugation under conditions where there is a positive charge in the π orbital of the aromatic ring. In this situation hyperconjugation constitutes a very powerful resonance effect with rigorous stereoelectronic requirements[25,80,88]—the breakdown of σ,π-conjugation (on passing to compounds where the Hg–C bond is located in the nodal plane of the π-electron system) diminishes the rates of certain electrophilic reactions by a factor of 10^8.[88]

An increase of the extent of σ,π-conjugation following the enhancement of the electron-donating properties of the substituents X has been established for systems with the cationic centre in the π-electron system (the compound $XHgCH_2C_6H_5$ under the experimental conditions according to electronic spectroscopic data for CTC)[80], which has been confirmed by ^{19}F NMR in the ground electronic state[89]. This constitutes convincing confirmation of Nesmeyanov's classical idea that the difference between the donor–acceptor properties of conjugated bonds has a significant influence on the hyperconjugation energy[21]. The negative ion mass spectra of σ,π-conjugated systems have a lower energy at the resonance maxima (destabilisation of the molecular orbitals due to conjugation) compared with the non-conjugated systems[76].

Thus Nesmeyanov's hypothesis[21,77] that the effect of σ,π-conjugation has a significant role in organoelemental compounds has been fully confirmed in a combined study of model derivatives of mercury[77].

We shall next consider data for hyperconjugation in compounds of silicon sub-group elements.

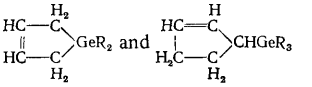
2. σ,π-Conjugation in Compounds of Silicon Subgroup Elements

The effect of σ,π-conjugation is clearly manifested in the study of compounds of silicon subgroup elements by vibrational spectroscopic methods[90–93]. An increase of the intensity of the bands corresponding to the vibration of the C=C bond and the vibration with a preferential extension of the $E-C_{all}$ bond as well as an increase of the degree of depolarisation of these bands have been observed in the Raman spectra of the compounds $(CH_3)_3ECH_2CH=CH_2$ (where E = C, Si, Ge, or Sn). On passing from silicon to tin, the exaltation of the molecular refraction in the allyl group increases. In the Raman spectra of the halogeno-derivatives Hal_3ECH_2. $CH=CH_2$ (E = Si or Ge), the intensity of the ν(C=C) line increases in the sequence F < Cl < Br and for fluoro-derivatives the line intensities are lower than for the methyl derivatives, which can be interpreted as a decrease of the extent of the σ,π-conjugation following the overall enhancement of the electron-accepting properties of the substituents R and the R_3ECH_2 fragment as a whole.

This conclusion as well as the conclusion that the σ,π-conjugation becomes more intense with increase of the atomic number of the element E on passing from Si to Ge and Sn evidently follows from the analysis of the highly characteristic out-of-plane vibrations of the $=CH_2$ group in the infrared spectra of the allyl derivatives[66,94] and has been confirmed by the study of the ^1H NMR spectra of the alkenyl derivatives of silicon and germanium[94]. Infrared spectroscopic study of a hydrogen bond of the type π...H–O– involving phenol indicates more pronounced π-donor properties of the allyl derivatives of silicon, germanium, and tin than for their carbon analogues. The differences between the electron-donating capacities cannot be accounted for by the differences between the electronegativities of the central atoms E. The increase of the electron density in the double bond with increase of the atomic number of E are a consequence of the increasing role of the σ,π-conjugation[95].

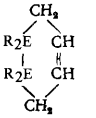
A method for the study of the electronic effects of the substituents at the π-donor centres (derivatives of ethylene, benzene, acetylene, etc.), which yields much information, is the electronic spectroscopy of charge-transfer complexes, for example, complexes of the π,π-type with tetracyanoethylene as the π-electron acceptor[96]. The principal spectroscopic parameter, the frequency of the charge-transfer band, contains information about the influence of the substituents not in the ground electronic state but in the charge-transfer state, where there is a positive charge in the π orbital of the donor. The presence of the charge can promote an increase of conjugation (including hyperconjugation) of typical electron-donating substituents of the +*M* type with the π-donor centre. Therefore in the state with charge transfer, modelling reaction systems with an ionic transition state [schemes of types (VII)–(IX)], the effect of σ,π-conjugation should be manifested most clearly[96]. This has been frequently confirmed experimentally for different compounds starting with the studies of Hanstein et al.,[23] Bock and Alt[24], and Pitt[25], and in particular for the allyl derivatives of silicon[97].

The fact that the electronic effects of the substituents R_3ECH_2 in $R_3ECH_2CH=CH_2$ are not limited to the inductive effect but include also a powerful σ,π-conjugation effect, which increases on passing from E = Si to E = Ge, is clearly manifested in the state with charge transfer[98]. A fairly strong σ,π-conjugation can occur only for a non-coplanar disposition of the E=C and C=C bonds, since this ensures a more effective overlapping of the electron clouds of the interacting bonds. Experimental confirmation of this fact has been obtained for allylsilane by infrared[99] and microwave[100] spectroscopic methods. In two compounds with the β-disposition of the germanium atom in relation to the C=C bond, i.e.



in the former (where the Ge–C and C=C bond are in the same plane) there is no hyperconjugation and in the latter (where the Ge–C bond deviates from the plane of the cyclopentene ring) the spectroscopic features of σ,π-conjugation are observed[101–103]. For the related silicon compounds, the stereospecificity of the σ,π-conjugation is shown just as clearly[104].

In contrast to sila- and germa-cyclopentenes having a planar ring structure, systems of the type



(E = Si or Ge) are non-planar and σ,π-conjugation in them has been established by vibrational and NMR spectroscopic methods[105]. In the electronic spectra of the trimethylallyl derivatives the absorption band near 55000 cm^{-1} (for E = C) undergoes a bathochromic shift and its intensity increases following a successive transition from carbon compounds to tin derivatives. According to the authors[106,107], these data indicate σ,π-conjugation in compounds of silicon subgroup elements, the extent of which increases with increasing atomic number not only in Group IV but also in the Periodic System as a whole. The cause of this phenomenon is apparently the more ready polarisability of the element with increase of its atomic number[107].

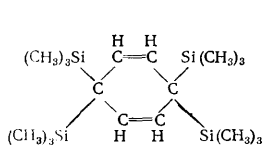
Important information about hyperconjugation has been obtained by photoelectron spectroscopy, which makes it possible to measure the vertical ionisation potentials[23], approximately equal to the energies of the corresponding molecular orbitals (with the sign reversed)[108]. In ethylene derivatives containing hydrocarbon substituents and their silicon-containing analogues, the highest occupied molecular orbital is of the π type[49,109]. The substituents $(CH_3)_3SiCH_2$ and H_3SiCH_2 increase the HOMO energy to a significant extent (the HOMO ionisation potentials are 9.0 and 9.49 eV)

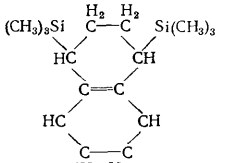
relative to the substituents $(CH_3)_3CCH_2$[49] and CH_3CH_2[110] (9.6 and 9.72 eV) as a consequence of the intense σ,π-conjugation in the silicon derivatives. The increase of the extent of σ,π-conjugation with increase of the atomic number of the Group IV element is accompanied by a further destabilisation of the π-type HOMO which is manifested by a decrease of the first ionisation potential[111,112] in trimethylallylgermane and trimethylallylstannane to ~ 8.8 and ~ 8.5 eV respectively (8.7 eV according to the data of Brown et al.[113]). The same conclusion concerning the influence of σ,π-conjugation on the ionisation potentials of HOMO have been reached using the mass-spectrometric method not only for trimethylallylsilane[114,115] but also for the disilyl derivatives of ethylene[116].

Thus the first vertical ionisation potentials, reflecting the influence of the substituents on the energy of the HOMO of the π type in the compounds *trans*-XHC=CHX when X is varied, are (in eV) 10.54 for H, 9.32 for $(CH_3)_3Si$, 8.99 for $(CH_3)_3C$, and 7.95 for $(CH_3)_3SiCH_2$.[116] The substituents X influence the HOMO energy via the inductive and conjugation mechanisms. Whereas the +*I* effect of the t-butyl group exerts the main influence on passing from X = H to $(CH_3)_3C$, when X changes from $(CH_3)_3C$ to $(CH_3)_3Si$, the $(p-d)\pi$ interaction (partial shift of the π electrons of the double bond to the unoccupied 3*d* orbitals of the silicon atom) has a dominant influence on the HOMO energy. This can be explained by the fact that the greater +*I* effect of the trimethylsilyl group compared with the t-butyl group (the inductive constants of these groups are respectively −0.9 and −0.3)[16] in the absence of the $(p-d)\pi$ interaction should have caused an increase of the ionisation potential in the disilyl derivative compared with its di-t-butyl analogue.

Judging from the ionisation potentials, the $(CH_3)_3SiCH_2$ group is the strongest donor although its σ* constant, amounting to −0.3,[66] is close to that of the t-butyl group and higher than the value for the trimethylsilyl group. The anomalously pronounced electron-donating properties of the substituents $(CH_3)_3SiCH_2$ are due to σ,π-conjugation. This effect increases regularly with increase of the number of substituents $(CH_3)_3SiCH_2$ at the double bond[117]. This is manifested experimentally by a decrease of the ionisation potentials, which are 7.7 eV for $CH_3[(CH_3)_3SiCH_2]C{=}C(CH_3).[CH_2Si(CH_3)_3]$ and 7.15 eV for $[(CH_3)_3SiCH_2]_2C{=}C[CH_2Si.(CH_3)_3]_2$, and also by an increase of the energy of the HOMO of the π type and the enhancement of the π-donor properties of the compounds[118]. The last compound does not form complexes with tetracyanoethylene of the usual type of olefins and the interaction involves the formation of radical-ion salts.

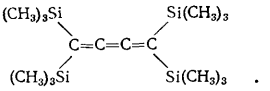
The following compounds have record low ionisation potentials[119]:


(7,00 eV)


(6,98 eV)

The large steric effects of the substituents at the multiple bonds make preferable the conformations of these molecules in which the Si–C bonds are arranged at right angles to the nodal plane of the olefin π-electron system, which ensures the most favourable conditions for σ,π conjugation. In the one-electron oxidation of a compound of this type, the products are radical-cations, which can be readily detected by EPR and which are stabilised as a result of σ,π-conjugation[118–120] (see also Bock and co-workers[121,122]).

An instructive example of the stabilisation of radical-ions by silicon-containing substituents is provided by butatriene derivatives:



The neutral silylbutatriene is unknown, but its radical-cation and radical-anion do exist[120]. Silylbutatriene formally contains π-electron systems of two types: the central ethylene bond and the butadiene system. The substituent $(CH_3)_3Si$ is a π-electron acceptor in relation to the butadiene system via the $(p-d)\pi$-interaction mechanism and therefore promotes the stabilisation of the radical-anions. The substituent $(CH_3)_3SiC\lesssim$ is an electron donor in relation to the ethylene bond via the σ,π-conjugation mechanism and stabilises the radical-cation[120]. The stabilisation of the radical-cation, sufficient for its detection by EPR at 220 K, confirms yet again the important role of σ,π-conjugation in systems with a positive charge in the π-electron system. The effective stabilisation of the radical-cations formed on electron transfer from allylsilanes via σ,π-conjugation with participation of an Si–C bond is an important factor in photochemical allylation reactions[123].

We shall now consider the σ,π-conjugation in the benzyl derivatives of silicon subgroup elements. It is known[22] that, as the substituent X in the ring, the $(CH_3)_3SiCH_2$ group exhibits anomalously pronounced electron-donating properties in electrophilic aromatic substitution reactions involving silicon derivatives of the type $(CH_3)_3SiC_6H_4X$. These properties cannot be accounted for by the inductive influence and they are related to the donation of electron density from $(CH_3)_3.SiCH_2$ to the ring via the σ,π-conjugation mechanism. With increase of the number of trimethylsilyl groups *n* in $[(CH_3)_3Si]_nCH_{3-n}Ar$ (where Ar = aryl), the degree of σ,π-conjugation also increases, which is indicated by the rates of cleavage of the Ar–Si bond in the compounds $[(CH_3)_3Si]_n.CH_{3-n}C_6H_4Si(CH_3)_3$ and the chemical shifts in the ^{19}F NMR spectra of the compounds p-$[(CH_3)_3Si]_nCH_{3-n}C_6H_4F$.[124] In the σ,π-conjugated systems in the transition state (and in its model consisting of a charge transfer state), there is a strong resonance interaction of substituents of the type R_3ECH_2 with the positively charged reaction centre. The constants σ^+, characterising the influence of the substituents in such a situation, indicate exceptionally marked electron-donating properties of R_3ECH_2, which become more pronounced with increase of the atomic number of E[23,96,125–128]. The accuracy of the determination of the constants σ^+ for organoelemental substituents depends on the quality of the initial correlation equations. The parameters of these equations differ somewhat when data for tens of compounds[125,126] and only a few compounds[23,127,128] are used. It has been suggested[128] that the accuracy of the initial equations and of the constants σ^+ increases when only a few compounds rather than tens of compounds are used. Although this view is not evident and requires special consideration, the order of magnitude of the quantities σ^+, established in a number of studies[23,125–128], makes it possible to place the substituents R_3ECH_2 in the same series with the strongest organic electron donors of the type of OAlk and $NAlk_2$.

Further investigation of the influence of σ,π-conjugation in the transition state[64,129,130] and comparison of the reactivities of benzyl derivatives of silicon subgroup elements with

the spectroscopic parameters of charge-transfer complexes of these compounds stimulated the study of the effects of organoelemental substituents in the ground electronic state of σ,π-conjugated systems. Thus the constants σ_R^0 (which characterise the conjugation of the substituent with the benzene ring) of the substituents R_3SiCH_2,[131] R_3GeCH_2,[126] and R_3SnCH_2,[131], calculated on the basis of infrared spectroscopic data, indicate marked electron-donating properties of these substituents in the ground electronic state due to the σ,π-conjugation.

The anomalously high intensity of the bands corresponding to the multiple bond vibration, the bathochromic shift of the ultraviolet bands, and exaltation of the molecular refraction have been observed in the vibrational spectra of benzyl derivatives of the type $R_3SiCH_2C_6H_5$ as well as allylsilanes[90]. Thus benzylsilanes exhibit the characteristic properties of σ,π-conjugated systems. This conclusion follows evidently also from the analysis of the ionisation potentials of wide series of benzene derivatives with silicon-containing substituents. The ionisation potentials and the approximate HOMO energies have been obtained by the mass-spectrometric method[114,115,132] from the frequencies of the charge-transfer bands in electronic absorption spectra of the complexes with tetracyanoethylene[17,24,25,80,115,133–136] and (the most accurate values) from photoelectron spectra[48,59,112,122,137,138].

The introduction of the $(CH_3)_3SiCH_2$ group into the benzene molecule entails a sharp decrease of the first ionisation potential (i.e. the destabilisation of the HOMO of the type) from 9.24 to 8.35 eV. The ionisation potentials of di- and tetra-substituted derivatives (in the 1- and 3- and 1-, 2-, 4-, and 5-positions) decrease further to 7.75 and 7.10 eV.[137] The ionisation potentials of the carbon analogues are significantly higher. For example, they are 8.25 and 7.75 eV for n-$(CH_3)_3CCH_2C_6H_4CH_2C(CH_3)_3$ and p-$(CH_3)_3SiCH_2C_6H_4CH_2Si.(CH_3)_3$.[122] Thus the large electron-donating effect of the trimethylsilylmethyl group increases as these groups accumulate in the molecule and hence there is an increase of the overall effect of σ,π-conjugation. This increase is not entirely additive, since the presence of several bulky $(CH_3)_3SiCH_2$ groups in the molecule prevents the establishment of the conformation most favourable for σ,π-conjugation. This is particularly marked for the *ortho*-disposition of the substituents and also for polysubstituted benzenes. Thus, on passing from the tetra- to the hexa-derivatives, there is no decrease but an actual increase of the ionisation potential from 7.10 to 7.40 eV.[137] The intense electron-donating properties of the trimethylsilylmethyl groups, comparable in their influence to the effects of the methoxy- or amino-substituents and increasing in the presence of a positive charge on the π-electron system, promotes the stabilisation of the radical-cations.

In the radical-cations formed from benzene derivatives containing substituents of the type $[(CH_3)_3Si]_nCH_{3-n}$ with ionisation potentials below 7.8 eV, the incorporation of one-electron oxidants can be readily detected by EPR[122,137–139]. Analysis of the parameters of the EPR spectra indicates (like the ionisation potentials of the initial compounds) the delocalisation of spin density over the substituting group and the existence of a preferred conformation of the radical-cations determined by steric factors and the degree of σ,π-conjugation[137–139].

It follows from the photoelectron spectra of the trimethylbenzyl derivatives of silicon, germanium, and tin that the ionisation potentials decrease steadily and the effect of σ,π-conjugation increases with increase of the atomic number of the silicon subgroup element[59,112]. Although it is difficult to estimate quantitatively the relative contributions of σ,π-conjugation and the +*I* effect to the overall electronic effect of the $(CH_3)_3ECH_2$ groups, there is no doubt (at least in systems with a positive charge in the π orbital) that σ,π-conjugation predominates[140], exerting a very marked influence on the rates of chemical reactions and stabilising effectively the carbonium ions.

A clear proof of the enhancement of the effect of σ,π-conjugation on benzyl derivatives has been obtained on comparing the π-donor properties of these compounds in the ground electronic state and in the charge-transfer state, i.e. in the presence of a positive charge in the aromatic ring[125,140–143]. The infrared spectroscopy of π...H–O hydrogen bonds between benzyl derivatives and phenol is used to investigate the π-donor properties in the ground state[144]. The parameter characterising the π-donor properties is the shift of the stretching vibration frequency of the bond involving phenol in the infrared spectrum ($\Delta\nu$) on formation of the hydrogen bond. As for the allyl derivatives of silicon subgroup elements, a steady enhancement of the π-donor properties is observed for the benzyl analogues with increase of the atomic number of E, which cannot be explained by the variation of the electronegativity of E and which reflects the enhancement of the σ,π-conjugation on passing from silicon to tin[125,144].

The same conclusion was also reached in the study of the electronic absorption spectra of charge-transfer complexes of benzyl derivatives with tetracyanoethylene[125,126,141,142] or iodine[143]. The charge-transfer frequency (ν_{CT}) characterises the π-donor properties of the given derivatives in the charge-transfer state, i.e. when, under the conditions of the electronic spectroscopic experiment, the electron from the HOMO, localised mainly in the aromatic ring, is almost fully transferred to an unoccupied orbital of tetracyanoethylene or iodine and a positive charge is formed in the HOMO of the π type. Analysis of the type of relation between $\Delta\nu$ and ν_{CT}[125,141] shows that the positive charge in the ring enhances the effects of the π,π-, *p*,π-, and σ,π-conjugations of the substituents with the ring.

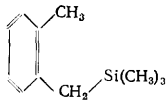
On transition to the state with charge transfer, a greater enhancement of the σ,π-conjugation is observed for the benzyl derivatives of germanium than for benzylsilanes[125,141].

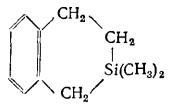
Systematic studies of the ^{13}C and ^{19}F NMR spectra of compounds containing the $(CH_3)_3ECH_2$ and $(C_6H_5)_3ECH_2$ fragments (where E = Si, Ge, Sn, or Pb), linked to the benzene or naphthalene ring and the biphenyl group, showed[19,145–147] that in the ground electronic state these fragments possess electron-donating properties and influence the π-electron system mainly via the σ,π-conjugation mechanism. The conjugation is intensified with increase of the atomic number of E in the sequence Si < Ge < Sn < Pb. (The effect of σ,π-conjugation in the benzyl derivatives $R_3SiCH_2C_6H_5$ has also been established by ^{29}Si NMR.[148])

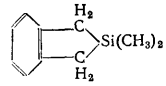
Yet another confirmation of the important role of hyperconjugation in organometallic compounds has been obtained by the joint application of the ^{13}C NMR and quantum-chemical methods[147]. A correlation has been established for derivatives containing the fragments $(CH_3)_3ECH_2$ (E = C or Sn) between the chemical shift difference in the ^{13}C NMR spectra of the tin and carbon compounds, on the one hand, and the change in the π-electron density, calculated by quantum-chemical methods, on passing from neutral to charged compounds modelling the intense conjugation of the substituent with the π-electron system, on the other. This correlation constitutes confirmation of the strong σ,π-conjugation of the $(CH_3)_3SnCH_2$ group with the benzene and naphthalene rings and the biphenyl group.

When the photoelectron spectroscopic data for benzyl derivatives were considered[137], the dependence of the degree of conjugation on stereoelectronic factors was noted above.

The influence of all these factors is clearly seen also from the Raman and NMR spectra. The characteristic features of σ,π-conjugation (high intensity of the band corresponding to the vibration of the multiple bond in the Raman spectra and exaltation of the molecular refraction) have been observed[149] for compounds (A) and (B) but not for compound (C).

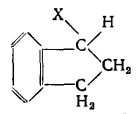

(A)


(B)

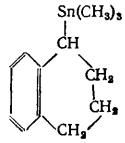

(C)

For the same compounds but with one fluorine indicator atom in the ring (instead of hydrogen), the above conclusion was confirmed by ^{13}C NMR[150] and ^{19}F NMR[151] methods. On passing to the bicyclic 2-silaindan (C), having a planar structure, from compound (A), the intense σ,π-conjugation in the latter breaks down owing to the disposition of the Si–C bond in the nodal plane of the π-electron system. In the conformationally non-rigid silatetralin (B), σ,π-conjugation becomes possible for certain conformations, but this effect is weaker than in compound (A).

The same conclusions were reached in the analysis of the ionisation potentials of these compounds and also of a number of organoelemental derivatives of indan[25]

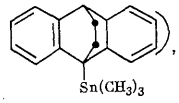

X=Si(CH$_3$)$_3$, Si$_2$(CH$_3$)$_5$, Ge(CH$_3$)$_3$

and indene[152]. In these compounds the angle between the E–C σ-bond and the π-electron system is ~ 30°. The ionisation potential of the π-electron system therefore increases steadily with increase of the atomic number of E[152] owing to σ,π-conjugation. When X = Sn(CH$_3$)$_3$ and also for another conformationally labile compound



the conformation in which the maximum σ,π-conjugation obtains is preferred according to ^{13}C NMR data[89].

If the Sn–C bond is fixed in the nodal plane of the π-electron system (as in the model compound



then there is no σ,π-conjugation[89], as in the organomercury compound with a related structure[88].

One cannot rule out the possibility that hyperconjugation obtains in the substituent–aromatic ring system in derivatives of benzene, naphthalene, and anthracene containing substituents of the type ER$_3$ bound directly to the π-electron system. The possibility, in principle, of hyperconjugation follows from both general considerations, described in the introduction, and from the theoretical examination of the problem (for example, by Pitt[17]).

Considerable difficulties are encountered in the experimental study of hyperconjugation of this type. When E=C, the above effect is apparently extremely small and is possibly absent in the ground electronic state[3,6–8]. For silicon compounds, hyperconjugation of the type considered (consisting in the transfer of electron density from R$_3$Si to the aromatic ring) is masked by the influence of the stronger effect of the $(p–d)\pi$ interaction acting in the opposite direction[20,67–70], the traditional explanation of the mechanism of which consists in the concept of the transfer of π-electron density from the aromatic ring to the unoccupied 3*d* orbitals of the silicon atom.

On successive transition from E = Si to Ge, Sn, and Pb, the $(p–d)\pi$ interaction weakens[20] and hyperconjugation should be intensified according to all the available literature data. However, even under the most favourable conditions for the study of hyperconjugation in systems of the type R$_3$E–Ar (i.e. for E = Sn or Pb), unambiguous experimental data supporting the occurrence of hyperconjugation have not been obtained. Thus detailed analysis of the parameters of the ^{13}C NMR spectra led the authors[153] to the conclusion merely that hyperconjugation is likely in the compounds R$_3$E–Ar, where E = Ge, Sn, or Pb. The conclusion that, of the two factors—hyperconjugation and $(p–d)\pi$ interaction—the former predominates in phenylsilane and trimethylphenylsilane, while the latter, discovered in the analysis of photoelectron spectra and by quantum-chemical calculations, predominates in trifluorophenylsilane[154], also appears ambiguous. Furthermore, numerous literature data, including those examined above as well as the results of a number of other studies[20,67–70], show that the SiR$_3$ fragments bound to the aromatic ring have electron accepting properties in relation to the groups CR$_3$, which is traditionally thought to be due to the $(p–d)\pi$ interaction.

Thus in compounds of the type R$_3$SiCH$_2$Ar the group R$_3$SiCH$_2$ (where R is an alkyl substituent) is a typical electron donor involving the σ,π-conjugation mechanism and also the inductive effect. The R$_3$Si fragment in the compounds R$_3$SiAr is a powerful electron donor operating via the inductive effect and is probably also a donor operating via the mechanism involving hyperconjugation with the ring, while, in terms of the mechanism involving the $(p–d)\pi$ interaction, this group is an electron acceptor.

The overall electronic effect of the R$_3$Si fragment is such that, compared with the isostructural carbon group R$_3$C, the silyl fragment is an electron acceptor in relation to the π-electron system. An unusual combination of the properties of the R$_3$SiCH$_2$ and R$_3$Si fragments is observed in the group R$_3$SiSiR$_2$ bound to the aromatic ring[143]. It is to be expected, firstly, that this group is as strong an electron donor as the R$_3$Si group in terms of the inductive effect. Secondly, like R$_3$Si, this group should exhibit electron-accepting properties in relation to the π-electron system of the aromatic ring in terms of the mechanism involving the $(p–d)\pi$ interaction. Thirdly, the R$_3$SiSiR$_2$ group, involved in σ,π-conjugation with the π-electron system, should exhibit electron-donating properties and the latter should be more marked than those of the R$_3$SiCH$_2$ group as a consequence of the higher polarisability of the Si–Si bond compared with Si–C. The overall electronic effect of the R$_3$SiSiR$_2$ group consists of the contributions listed above. It is therefore difficult to estimate *a priori* the resultant electronic effect of the R$_3$SiSiR$_2$ and R$_3$SiCH$_2$ groups relative to π-electron systems.

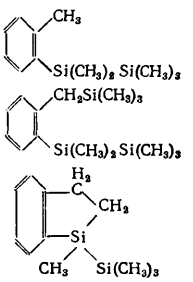
We shall now consider experimental data referring to systems of the type R$_3$SiSiR$_2$–Ar. Pentamethylphenyldisilane, its derivatives, and related compounds, as well as their complexes with tetracyanoethylene have been studied systematically by electronic spectroscopy (see Sakurai's review[155]). It was established that the Si–Si bond is involved in conjugation with the benzene ring and the multiple bond[155–161]. Whereas in the initial study the mechanism of the conjugation

was believed to involve the unoccupied 3*d* orbitals of the silicon atom[159], subsequently the important role of the σ,π-conjugation of the σ orbitals of the Si–Si bond with the π-electron system was established[155,162,163].

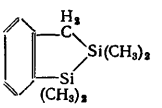
In relation to the benzene ring, the $Si(CH_3)_3Si(CH_3)_2$ group behaves as an electron donor in terms of the overall electronic effect, although its electron-donating properties are weaker than those of the $(CH_3)_3SiCH_2$ fragment[155]. This conclusion, reached in the analysis of the ultraviolet spectra, has been confirmed from σ^+ and σ^- constants for the group $Si(CH_3)_3Si(CH_3)_2$ determined by infrared and NMR spectroscopy[164,165]. These constants indicate a typical electron-donating character of the $Si(CH_3)_3Si(CH_3)_2$ group compared with $Si(CH_3)_3$ owing to σ,π-conjugation with participation of the Si–Si bond, although the numerical values of the constants require revision. The increase of the number of trimethylsilyl groups in the sequence $Si(CH_3)_2Si(CH_3)_3$ < $Si(CH_3)[Si(CH_3)_3]_2$ < $Si[Si(CH_3)_3]_3$ is accompanied by an enhancement of the electron-donating properties of the group characterised by the constant σ^+.[165] On the other hand, the trimethylsilyl and pentamethyldisilyl groups exhibit in the ground electronic state similar electron-accepting properties in relation to the ring[164].

The dual functions of the $Si(CH_3)_3Si(CH_3)_2$ group [electron-donating as a consequence of σ,π-conjugation and electron-accepting due to the $(p-d)\pi$ interaction] make it possible to understand[143] the regularities in the electronic absorption spectra of the charge-transfer complexes of π-donors containing this and similar groups[24,162,163,166-169] as well as the variation of the ionisation potentials of π-electron systems containing disilyl substituents[48,162,163,166]. The weaker electron-donating properties of the $Si(CH_3)_3Si(CH_3)_2$ fragment compared with $(CH_3)_3SiCH_2$ are not a result of the decrease of the effect of σ,π-conjugation with participation of the Si–Si bond (as was believed, for example, by Sakurai and Kira[163]) but are a consequence of the competition between two opposed conjugation effects [of the σ,π- and $(p-d)\pi$-types] in disilyl derivatives. If only the effect of σ,π-conjugation operated, then, owing to the greater polarisability of the Si–Si bond compared with Si–C, the disilyl fragment would have exhibited more pronounced electron-donating properties than the $(CH_3)_3SiCH_2$ fragment.

A test of the fulfillment of the stereoelectronic conditions for σ,π-conjugation by ultraviolet spectroscopy showed[169,170] that the compounds

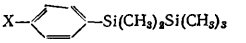


and a number of their analogues[169] have ultraviolet spectra characteristic of systems with σ,π-conjugation. On the other hand, in a compound of the type



the conjugation is weakened[169], while according to other data[170] it is altogether absent.

Important information about the characteristic features of σ,π-conjugation is provided by the analysis of the character of the HOMO of pentamethylphenyldisilane. The ionisation potential of the π electrons of the Si–Si bond (8.69 eV) in hexamethyldisilane[171] is lower than the ionisation potential of the π electrons of benzene (9.24 eV). The HOMO of pentamethylphenyldisilane, which is a linear combination of the symmetrical HOMO of benzene and the molecular orbital of the Si–Si σ-bond, contains a dominant contribution by the σ orbital of the Si–Si bond (72% according to quantum-chemical calculations[166]). As a result of this, the long-wavelength absorption bands in the electronic spectra of the charge-transfer complexes of phenyldisilanes[155,162,163,166] and vinyldisilanes[98] with tetracyanoethylene are assumed to involve intermolecular charge transfer from an orbital of the σ(Si–Si) type, like the bands in the spectra of complexes of methylpolysilanes[172,173]. The contribution of the σ(Si–Si) orbital to the HOMO of the compounds



depends on the nature of X and increases with enhancement of the electron-accepting properties of X.[166] From the standpoint of classical ideas about hyperconjugation, this can be interpreted as the intensification of the direct polar conjugation between the substituents $Si_2(CH_3)_5$ and X (or the intensification of the σ,π-conjugation of the Si–Si bond with the π-electron system) as the electron-accepting properties of the substituent X become more marked [Schemes (IV), (VII), and (X)].

Thus the effect of σ,π-conjugation has been studied in fair detail for derivatives of benzene and ethylene. The literature data on this effect involving other π-donor centres are limited but are consistent with the data for benzene and ethylene derivatives.

Thus the Si–Si fragments exhibits electron-donating properties via the σ,π-conjugation mechanism not only in relation to the benzene ring but also in relation to the double bond as well as the cyclopentadienyl ring, which follows from the EPR spectra of the cyclopentadienyl and silylcyclopentadienyl free radicals[174].

The effect of σ,π-conjugation in h^1-cyclopentadienyl derivatives $C_5H_5ER_3$ leads to a decrease of the ionisation potentials with increase of the atomic number of E on passing from silicon to tin[175], can influence the angles between the E–C bonds and the average planes of the rings[176,177] (although the structure of compounds of this type is still the subject of discussion[178]), and is also manifested in a series of other physicochemical properties[175].

The study of naphthalene derivatives by NMR[19,145,147], ultraviolet spectroscopy[162], the ultraviolet spectroscopy of charge-transfer complexes with tetracyanoethylene[160,162,163], and polarography[162] has shown that the substituent $(CH_3)_3SiCH_2$ is involved in σ,π-conjugation with the ring[19,145,147,160,162,163] and the overall electronic effect of the $Si(CH_3)_3$.$Si(CH_3)_2$ group is less electron-donating than the influence of the trimethylsilylmethyl group[162,163]. It has been shown[162,163] that the HOMO pentamethylnaphthyldisilane is a linear combination of the π-type HOMO of naphthalene and the molecular orbital of the Si–Si σ-bond. However, in contrast to the corresponding disilyl derivative of benzene[166], the HOMO in the naphthalene derivative has a preferential π character[162,163], since the ionisation potential of the π electrons of naphthalene (8.11 eV)[179] is lower than that of the π electrons of benzene (9.24 eV) and the σ electrons of the Si–Si bond (8.69 eV)[171]. The increase of the atomic number of E on passing from Si to Pb intensifies the σ,π-conjugation of the R_3ECH_2 fragment with the naphthalene

ring[19,145]. According to electronic spectroscopic data for complexes with tetracyanoethylene[180], the $(CH_3)_3SiCH_2$ fragment linked to the furan ring also exhibits anomalously pronounced electron-donating properties due to σ,π-conjugations which cannot be accounted for by the inductive effect.

Analysis of the positions and intensities of the absorption bands in the electronic spectra of 2-substituted pyridines[181] indicates the intensification of the σ,π-conjugation with increase of the atomic number of the element E in the $(CH_3)_3.ECH_2$ fragment and also on passing from substituents of the type $(CH_3)_3ECH_2$ to $[(CH_3)_3E]_2CH$. On the other hand, the diminution of the electron-donating properties of three substituents of the atom E, for example, on passing from $CH_2Si(CH_3)_3$ to the silatranyl derivative $CH_2Si(OCH_2CH_2)_3N$,[182]

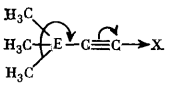
is accompanied by a weakening of σ,π-conjugation.

A significant role of effects of the type of π,π- and p,π-conjugation in acetylene derivatives has been noted in the literature[14]. According to Muller's estimates[9], hyperconjugation, treated as one of the conjugation effects, should be twice as intense on conjugation with a triple bond [Schemes (III), (VI), (IX), (XII), (XV), (XVIII), (XXI), and (XXIV)] as in conjugation with a double bond [Schemes (II), (V) (VIII), (XI), (XIV), (XVII), (XX), and (XXIII)]. This powerful influence of hyperconjugation on the properties of acetylenes is clearly manifested in organoelemental derivatives. Among all the π-donors investigated (derivatives of benzene[115], naphthalene[162,163], furan[180], thiophen[183], pyridine[181], ethylene[98,115], and buta-1,4-diene[115]), only acetylene derivatives exhibit anomalies in the character of the influence of substituents of the type $(CH_3)_3C$, $(CH_3)_3Si$, and $(CH_3)_3SiCH_2$.[115,184]

The substituents can usually be arranged in the sequence $(CH_3)_3Si < (CH_3)_3C < (CH_3)_3SiCH_2$ in terms of their electron donating properties in relation to the π-electron system. The diminution of electron-donating properties in $(CH_3)_3Si$ compared with $(CH_3)_3C$ in accordance with the above sequence is traditionally attributed to the influence of the electron-accepting (relative to the π-electron system) effect of the $(p-d)\pi$ interaction and the enhancement of the electron-donating properties of the $(CH_3)_3SiCH_2$ group relative to $(CH_3)_3C$ is due to σ,π-conjugation. If the possibility of effective hyperconjugation with a π-donor centre is ensured for the substituent $(CH_3)_3Si$ (this is apparently never attained for aromatic compounds and ethylene derivatives, as stated above), then the positions of the substituents $(CH_3)_3Si$ and $(CH_3)_3C$ in the series based on the electron-donating properties can change.

The inversion of the usually observed electron-donating order has been established as an experimental fact[115,184] for the acetylenes $HC\equiv CR$, where the electron-donating properties of the substituents R vary in the sequence $(CH_3)_3C < (CH_3)_3Si < (CH_3)_3SiCH_2$. On the other hand, judging from the charge-transfer frequency in the electronic spectra of the complexes of tetracyanoethylene[185], the usual sequence based on the electron-donating properties of the substituents is observed for the phenylacetylenes $C_6H_5C\equiv CR$. In the disubstituted derivatives $R-C\equiv C-R$ and $R-C\equiv C-C\equiv C-R$, the electron-donating properties of R also lead to the usual sequence $(CH_3)_3Si < (CH_3)_3C < (CH_3)_3SiCH_2$,[184] while the methyl group at the triple bond is a stronger donor than the silyl group[186].

The study of a wide range of silicon-, germanium-, and tin-containing acetylenes and their carbon analogues established the important role of hyperconjugation in organoelemental derivatives not only in the charge-transfer state (with a positive charge on the π-donor centre—electronic spectroscopy of the iodine complexes) but also in the ground state (infrared spectroscopy of the hydrogen bond with phenol)[187]. The hyperconjugation



is intensified with increase of the atomic number of E in the sequence Si < Ge < Sn and with enhancement of the electron-accepting properties of the substituents X. When the donor–acceptor properties of the substituents $(CH_3)_3E$ and X are equalised, the intensity of the hyperconjugation diminishes sharply but in compounds of the type $(CH_3)_3E-C\equiv C-E'(CH_3)_3$, i.e. when $X = E'(CH_3)_3$, it still remains fairly effective. Despite the similar donor–acceptor properties of the substituents $(CH_3)_3E$ and $(CH_3)_3E'$, the high polarisability of the atoms E' and E (silicon, germanium, and tin) and of the triple bond as well as the high sensitivity of the acetylenic π-electron system to the electronic effects of the substituents favour hyperconjugation in acetylene derivatives containing two silicon subgroup elements attached to the triple bond[187].

Thus, in compounds with the fragments $\geq E-\overset{|}{C}-X$ or $\geq E-\underset{|}{E}-X$ (E is a silicon subgroup element and X is an aromatic ring or a multiple bond), the interaction between the E—C and E—E bonds and the group X involves a σ,π-conjugation mechanism. The effect operates in the direction from the element E to the group X. If the substituent X is an atom with unshared electron pairs, then the mechanism of the interaction between E and X changes fundamentally[69] and involves the transfer of electron density in the direction from X to E (see the relevant reviews[188,189]). The traditional treatment of the interaction between X and E involves in this instance the concept of intramolecular coordination with participation of the unshared electron pairs of X and the unoccupied *nd* orbitals of the atom E,[190] but there exist also alternative approaches[191].

Apparently in certain systems there is a possibility of both types of interaction. This probably cannot be ruled out for silyl ketones where the presence of the C=O double bond and of the unshared electron pair of the oxygen atom is responsible for the complexity of the intramolecular interactions and the ambiguity of the conclusions concerning hyperconjugation[160,192,193]. Both intramolecular coordination and hyperconjugation apparently occur in cyclic silyl- and germyl-ketones[194].

3. The σ,σ- and σ,*p*-Conjugation in Compounds of Silicon Subgroup Elements

The effect of σ,σ-conjugation is a specific feature of organometallic compounds to an even greater extent than that of σ,π-conjugation. Systematic studies of the effect of σ,σ-conjugation have not been published and the few data available on this question can be consistently interpreted mainly in those cases where σ,σ-conjugation influences the reactivity of organometallic compounds in the transition state. Many clear examples of such influence have been quoted by Nesmeyanov[21,71], who established, in particular, a fairly profound analogy between the properties of the conjugated systems (π,π-, *p*,π-, σ,*p*-, σ,π-, and σ,σ-) which makes it possible to treat them from the same general standpoint[9]. It follows from the last conclusion that the absence of fundamental discrepancies with the rules established for

other conjugated systems constitutes an indirect confirmation of the validity of the conclusions reached in the study of σ,σ-conjugation in the ground electronic state.

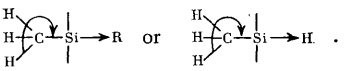
On the basis of the proton chemical shifts in the methyl groups in the ^{1}H NMR spectra of the tetramethyl derivatives $(CH_3)_4E$, Allred and Rochow[15] proposed an electronegativity scale for Group IV elements: C(2.60) > Pb(2.45) > Ge(2.00) > Sn(1.93) > Si(1.90). It was then postulated that there is a possibility of hyperconjugation in the tetramethyl derivatives $\rangle E^- = CH_2H^+$, but the authors assumed that this effect should be equally important for all the compounds of silicon subgroup elements. (In Section II it was noted that the occurrence of hyperconjugation in tetramethylsilane follows from quantum-chemical calculations[62].) According to Allred and Rochow[15], hyperconjugation should therefore make a constant contribution to the electronegativities.

Criticism of the Allred–Rochow electronegativity scale by Egorov[195] was based on the fact that this scale is not only a measure of the inductive effect but also includes the so called *C* effect and hyperconjugation. However, we believe that the *C* effect and hyperconjugation are synonymous terms. Indeed, analysis of the vibrational spectra established that an electron-accepting *C* effect is characteristic of the E atoms, increasing monotonically on passing from silicon to germanium and tin[195]. The presence of this effect has been demonstrated sufficiently rigorously only for methyl derivatives and the nature of the *C* effect has not been elucidated. Bearing in mind that hyperconjugation in methyl derivatives (like σ,π-conjugation in benzyl derivatives) does not constitute a constant contribution but increases in the sequence Si < Ge < Sn < Pb with increasing polarisability of the elements E, the conclusion that the terms "*C* effect" and "hyperconjugation" describe the same electronic σ,σ-conjugation effect becomes evident.

The concept of hyperconjugation has been used in the interpretation of the infrared and ^{1}H NMR spectra of silane[196] and stannane[197] derivatives. In the absence of extreme steric effects of the substituents[198], the frequency ν of the highly characteristic stretching vibration of the Si–H bond in the vibrational spectra of R_3SiH depends almost exclusively on the electronic effect of the substituents R.[199] If there are no resonance effects, then the frequency depends only on the inductive effect of R. However, the equation relating ν and the inductive constants σ* of the substituents R has an insufficiently high correlation coefficient. The frequency ν decreases when R is varied in the sequence CH_3 > iso-C_4H_9 > H = C_3H_7 ≅ n-C_4H_9 ≅ C_2H_5 > iso-C_3H_7; this series deviates from the σ* constant scale apparently owing to σ,σ-conjugation[196]. Shielding of the hydrogen atom in the Si–H group increases in the following sequence according to ^{1}H NMR spectra: CH_3 ≅ iso-C_4H_9 < n-C_4H_5 < C_2H_5 < iso-C_3H_7. The explanation[196] of the discrepancy between this sequence and the variation of the constants σ* by σ,σ*-conjugation is not quite so unambiguous in the given instance (as in the case of the frequencies ν), since the shielding revealed by ^{1}H NMR spectra can involve contributions due to magnetic anisotropy, which mask the donor–acceptor effects of the substituents.

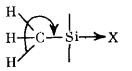
According to the ^{1}H NMR spectra of the stannane derivatives R_3SnH, R_2SnH_2, and $RSnH_3$, hydrogen atom shielding in the Sn–H group increases in the sequence iso-C_3H_7 < n-C_4H_9 ≅ n-C_3H_7 ≅ C_2H_5 < CH_3 and the frequencies of the stretching vibrations of the Sn–H bond in the infrared spectra of the methyl derivatives are anomalously high and are close to those for the phenyl derivatives. This also indicates the presence of hyperconjugation, which is particularly pronounced for the methyl derivatives[197]. An anomalously high frequency ν(Ge–H) is also observed in the infrared spectrum of trimethylgermane compared with other trialkylgermanes[200]. The greater role of σ,σ-conjugation in organogermanium compounds compared with organosilicon compounds is apparently the main cause of the higher intensity of the ν(Ge–H) bands compared with ν(Si–H) in the infrared spectra of compounds of the type R_3EH having an analogous structure (where E = Si or Ge)[201].

A semiquantitative estimate of the effects of σ,σ-conjugation has been made for the methyl derivatives of silicon. As mentioned above, the frequencies ν(Si–H) in the infrared spectra of the compounds R_3SiH depend mainly on the inductive effect of the substituents R. If R is not involved in strong conjugation with the silicon atom [of the type of $(p-d)\pi$ interaction], then the equation $\nu_{ind} = 23.1\Sigma\sigma^* + 2112$ holds[199]. Although the frequency ν is in fact influenced by σ,σ-conjugation, the inductive effect makes a dominant contribution to ν. The low contributions of σ,σ-conjugation are due to the fact that the substituents R, which exert only an inductive effect, have as a rule small inductive constants and the difference between the donor–acceptor properties of the conjugated bonds in compounds with such substituents R is therefore small and the extent of hyperconjugation is likewise slight:



Nevertheless the dipole moment of the Si–C bond in methylsilane has the direction $H_3C \rightarrow SiH_3$.[202]

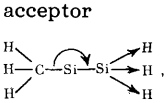
The introduction into the molecule of the substituents X forming $(p-d)\pi$ bonds with the silicon atom (and exerting a powerful inductive $-I$ effect) reduces the experimental values of ν_{exp} compared with ν_{ind}. The difference $\Delta\nu = \nu_{ind} - \nu_{exp}$ characterises the conjugation effects and for the methyl derivatives is smaller than for the ethyl derivatives. The effect of σ,σ-conjugation



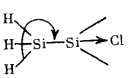
operates in opposition to the $(p-d)\pi$ interaction and the decrease of Δν for the methyl derivatives is a result of the stronger σ,σ-conjugation than for the ethyl derivatives[203–207].

Careful analysis taking into account the magnetic anisotropy of chemical bonds shows that, in terms of the ^{1}H NMR spectra, hyperconjugation decreases the shielding of the methyl protons compared with the CH_2 protons in the ethyl group[203]. The high polarisability and low ionisation potential of the silicon–silicon bond lead to extremely specific properties of polysilanes[208], which has been noted, in particular, in the study of σ,π-conjugation involving the pentamethyldisilyl group[143]. σ,σ-Conjugation is also manifested to an appreciable extent in polysilanes[209].

Depending on the nature of R in R_3SiSiH_3, the inductive constants σ* of the groups SiH_3, calculated on the assumption that only the inductive effect operates in disilanes, assume unrealistic values in the range from +1.5 to −1.5. As a partner in σ,σ-conjugation, the substituent R_3Si regulates the donor–acceptor properties of the silyl group which can function both as an acceptor

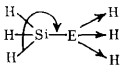


and as a donor



in hyperconjugation[209].

Thus, as for acetylene derivatives containing two organoelemental substituents[187], the variable contributions from σ,σ-conjugation impose fundamental limitations on the possibility of calculating the inductive constants of organoelemental substituents from infrared spectroscopic data for polysilanes. This applies equally to compounds of the type

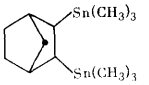


where σ,σ-conjugation becomes more intense on passing from E = Ge to E = Sn.[209]

The study of the ionisation potentials of cyclopropylmethyl-(trimethyl)stannane, allyltrimethylstannane, and a series of related compounds by photoelectron spectroscopy established[113] low values of the potentials in the first compound as a result of the σ,σ-conjugation of the C–Sn bond with the cyclopropane ring and in the second compound as a consequence of σ,π-conjugation. The similar energies of the σ,σ-interaction (1.6 eV) and the σ,π-interaction (2.2 eV) are consistent with the results of a study of silicon-containing derivatives of benzene, ethylene, and cyclopropane by the electronic spectroscopy of their iodine complexes[210]. This observation has been checked in order to compare the characteristics of σ,π- and σ,σ-conjugations.

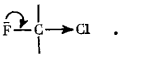
The presence of a positive charge on the cyclopropane and benzene rings as well as the double bond in the charge-transfer state leads to a qualitative indistinguishability of the characteristic features of the conjugation in all three systems[210]. We may note that in small strained cyclic systems of the type of bisbicyclobutane hyperconjugation plays an appreciable role also in the absence of organoelemental substituents[211].

Theoretical study[17] and experiments on photoelectron spectroscopy[212] indicate the interaction of the E–C σ-bonds via the σ,σ-conjugation mechanism in compounds of the type $(CH_3)_3ECH_2CH_2E(CH_3)_3$, where E = Si or Sn. The ionisation potentials of these compounds are appreciably lower than those of the related compounds where there is no hyperconjugation and the example of the compound



with rigidly fixed C–Sn bonds emphasises the importance of the stereoelectronic factors not only for σ,π-conjugation but also for σ,σ-conjugation[212].

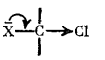
Systematic studies of the effect of σ,*p*-conjugation have not been made and most of the existing data have been obtained by the NQR method for chloro-derivatives of carbon and silicon subgroup elements. It is known, for example[213], that the frequencies in the ^{35}Cl NQR spectra of compounds of the type Cl–X increase with increasing electronegativity of X. The frequency therefore increases with increase of *n* in compounds of the type CCl_nH_{4-n}. As a consequence of the greater electronegativity of fluorine compared with chlorine, the increase of *n* in CF_nCl_{4-n} should also increase the frequency of the ^{35}Cl NQR signal, but the frequency is in fact somewhat reduced[213]. In order to account for this anomaly, which cannot be interpreted in terms of the inductive effect (electronegativity), the author[214] resorted to the concept of σ,*p*-conjugation:



As a result of the conjugation, the electron-accepting properties of the fluorine atom are diminished and the frequency of the ^{35}Cl NQR signal decreases compared with the value anticipated if only the inductive effect of the fluorine atom operated. Subsequently it was established[215] that hyperconjugation intensifies when fluorine atoms accumulate in the molecule. These problems were examined in greater detail by Semin et al.[213]

The initial data concerning σ,*p*-conjugation were developed significantly and generalised in the analysis of the ^{35}Cl NQR spectra of the compounds $R'R''R'''CCl$.[213,216–218] The compounds were combined in two groups. The first group included compounds whose substituents R did not contain unshared electron pairs. The NQR frequencies of these derivatives are linearly related to the sum of the inductive constants of the three substituents R: $\nu = 33.9 + 10.64\Sigma\sigma_I$. The compounds of the second group have R with unshared electron pairs (F, Cl, Br, I, or O) and their NQR frequencies deviate from the linear relation towards lower values. The deviation Δ is linked by the relation $\Delta = 13.32\Sigma\sigma_R$ with the sum of the constants σ_R characterising the capacity of R for conjugation.

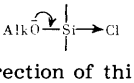
The two-parameter equation $\nu = 33.9 + 10.64\Sigma\sigma_I + 13.32\Sigma\sigma_R$ indicates an important role of the effects of σ,*p*-conjugation



in carbon compounds[213,219,220]. According to classical ideas concerning hyperconjugation, when the electron-accepting properties of the chlorine atom remain unchanged, the σ,*p*-conjugation intensifies (Δ increases) as the electron-donating properties of the atom with unshared electron pairs are enhanced (the constants σ_R increase).

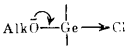
Systematic study of the dependence of the ^{35}Cl NQR frequencies on the electronic effects of the substituents in chlorosilanes[217] and chlorogermanes[220] showed that the inductive effect of the substituents is not the only cause of the changes in the frequencies[213,218,221,222]. Statistical treatment of the literature data on the frequencies of the ^{35}Cl signal in the spectra of $(R_1)_3E–Cl$[223] established the significance of the resonance effects.

At the same time the interpretation of the resonance effects within the framework of σ,*p*-conjugation was not found to be quite as evident as for the carbon compounds. Thus the extent of σ,*p*-conjugation in organosilicon compounds



and probably also the direction of this effect[221] depend greatly on the nature of the two other substituents at the silicon atom. The effect of σ,*p*-conjugation is observed for compounds in which the substituents exert the maximum influence on the central silicon atom via the $(p–d)\pi$ conjugation and inductive mechanisms. Significant changes in the positive charge on the silicon atom and of the bond polarities apparently influence greatly the extent of σ,*p*-conjugation, but this problem has not so far been studied. It is believed that such studies permit a deeper understanding of the relative contributions of σ,*p*-conjugation and electrostatic interaction, the latter being sometimes put forward as an alternative to the former[222].

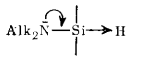
The ^{35}Cl NQR frequencies in the spectra of alkoxychlorogermanes are lower[222] than might have been expected on the basis of the inductive effect alone[213]. As in the case of alkoxychlorosilanes and the corresponding carbon derivatives, we believe that this is caused by σ,*p*-conjugation:



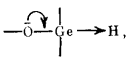
In the infrared spectroscopic study of compounds where the existence of σ,p-conjugation can be postulated[204,224-226], the possibility of interpreting the experimental data within the framework of the inductive effect and the $(p-d)\pi$ interaction alone was demonstrated. This conclusion was also reached in the analysis of the dependence of the frequencies and intensities of the highly characteristic stretching vibrations of the Si–H and Ge–H bonds in the infrared spectra on the electronic effects of the three substituents at the atoms E. The frequencies ν(Si–H) confirmed the presence of σ,p-conjugation in alkoxychlorosilanes[204] and chlorodimethylaminosilanes[224]



and also in silanes of the type Alk_2NSiH_3 and $(Alk_2N)Alk_2.SiH$.[224] The effect of σ,p-conjugation in compounds of the latter type



is possible in view of the exceptionally high capacity of dialkylamino-groups for conjugation, including hyperconjugation. The polarity of the Si–H bond in dialkylaminosilanes increases as a consequence of σ,p-conjugation, which is clearly manifested in the intensities of the Si–H bands in the infrared spectra[225]. The anomalous increase of the intensities of the stretching vibration bands of the Ge–H bond as a result of σ,p-conjugation in compounds containing the fragments



has been established[226].

Thus the studies of hyperconjugation in organic derivatives of silicon subgroup elements by spectroscopic methods resulted in the accumulation of fairly extensive experimental data concerning mainly σ,π-conjugation. The principal characteristics of σ,π-conjugation, confirmed by quantum-chemical methods (the sharp intensification of the effect on passing from carbon compounds to silicon derivatives and its further intensification with increase of the atomic number of silicon subgroup element; the dependence on the stereoelectronic factors which in the limiting cases determine the very possibility of hyperconjugation; the significant dependence of the magnitude of the effect on the difference between the donor–acceptor properties of the conjugated bonds and the possibility of regulating these properties by varying the substituents at the donor and acceptor fragments of the molecule; the intensification of the effect in the presence of a positive charge on the π-electron system) are not only features of the ground electronic state but also the most important factors which determine the reactivity of σ,π-conjugated compounds.

The effects of σ,σ- and σ,p-conjugation have been so far inadequately investigated. However it is of fundamental importance that the same features which are characteristic of σ,π-conjugated compounds are observed in σ,σ- and σ,p-conjugated systems. The hypothesis of a major role of hyperconjugation in organoelemental compounds and of a profound analogy between the conjugation effects in general, which was put forward 35 years ago[21,71], is thereby fully confirmed.

In future studies of hyperconjugation in organoelemental compounds, derivatives of Group IV elements and mercury will probably play the role of model systems. The characteristics of the hyperconjugation in these model systems are important both for the solution of the overall problem of the relation between the structure and reactivity of organoelemental compounds and for the investigation of many specific problems, for example of the role of σ,p-conjugation and other resonance effects in organoelemental compounds, the characteristics of the influence of σ,σ-conjugation in the ground and excited electronic states, and the role of hyperconjugation in compounds with a chain of metal atoms and highly polarisable chemical bonds.

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Institute of Chemistry,
USSR Academy of Sciences,
Gorky

Translated from *Uspekhi Khimii*, 53, 802-824 (1984) U.D.C. 547.1.118

Exchange Reactions in the Chemistry of Organophosphorus Compounds

P.S.Khokhlov

The results of studies of reactions involving the exchange of alkoxy-, aryloxy-, acyloxy-, phosphorus-containing, amino-, alkylthio-, arylthio-, and hydrocarbon groups between phosphorus compounds are surveyed. The influence of the structure of the organophosphorus compounds, the role of catalysis, and the available information about the mechanisms of these reactions are considered.
The bibliography includes 229 references.

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I. INTRODUCTION

Exchange reactions are important in the chemistry of organophosphorus compounds (OPC). Some of them serve as a basis for convenient methods of synthesis of OPC, while others occur in side processes during the preparation, isolation, and storage of OPC. The exchange reactions assume particular importance as a procedure for the introduction of a radioactive label into physiologically active OPC. The study of exchange reactions is also of interest from the standpoint of estimating the stability of OPC and of discovering the pathways in their chemical and metabolic transformations. The exchange reactions with participation of OPC are also of interest from the theoretical standpoint.

The study of exchange reactions involving OPC was developed greatly particularly during recent years, which has been partly reflected in a monograph[1]. However, the reviews on the exchange reactions of OPC [2,3] cover the literature only up to 1968 and are not exhaustive. The intramolecular exchange reactions involving OPC, induced by the migration of substituents in molecular rearrangements, have been adequately surveyed in a number of communications[4-7].

This review deals with intermolecular exchange reactions at the phosphorus atom which proceed without a change in its coordination number.

II. INTERMOLECULAR EXCHANGE OF ORGANIC SUBSTITUENTS IN PHOSPHORUS COMPOUNDS

The tendency of organophosphorus compounds to undergo exchange reactions is determined primarily by the mobility of the bond between phosphorus and the exchanging group, which depends both on the environment of the phosphorus atom and on the structure of the exchanging group; organic substituents linked to phosphorus via heteroatoms exchange more readily. Accordingly, it is useful to consider the OPC exchange reactions after subdividing them in terms of the types of exchanging groups.

1. Exchange of Alkoxy- and Aryloxy-Groups

The reactions involving the exchange of alkoxy-groups between phosphorus compounds and the isotypical reactions in which aryloxy-groups are exchanged have been subjected to most fundamental investigations in the series of derivatives of tricoordinate phosphorus. With rare exceptions, the alkoxy-groups in isotypical OPC exchange more readily than the aryloxy-groups.

Trialkyl phosphites enter into exchange reactions with PCl_3 merely on mixing the reactants[8]. In a mixture of triethyl phosphite with PCl_3 at 20°C, equilibrium is established after two days and faster on heating[9]:

$$(C_2H_5O)_3P + PCl_3 \rightleftarrows (C_2H_5O)_2PCl + C_2H_5OPCl_2 .$$

The kinetic characteristics of this and other exchange reactions of OPC have been published in a review[2].

Alkyl phosphorodichloridites, formed in the reaction of trialkyl phosphites with PCl_3, interact under similar conditions with the initial trialkyl phosphites to form dialkyl phosphorochloridites[10]:

$$(C_3H_7O)_3P + C_3H_7OPCl_2 \rightleftarrows 2(C_3H_7O)_2PCl .$$

The composition of the products of the exchange reactions between trialkyl phosphites and phosphorus trihalides therefore depends on the ratio of the initial reactants. The main products of the reactions of trialkyl phosphites with PCl_3, taken in molar proportions of 2 : 1, are dialkyl phosphorochloridites, which are in fact mainly obtained by this procedure[11-19]:

$$2\,(RO)_3P + PCl_3 \rightarrow 3\,(RO)_2PCl ;$$
$$R=CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9,\ C_8H_{17},\ C_{12}H_{25},\ C_3H_5OC(O)CH_2 .$$

The composition of the exchange products and the rate of reaction depend to some extent also on the electron density at the phosphorus atom and on the structure of the ester groups. In the series of trialkyl phosphites the rate of exchange depends little on the length of the alkoxy-groups. Thus the reactions of the lowest trialkyl phosphites with PCl_3 reach completion comparatively rapidly at 20 °C, while the analogous reaction of tridodecyl phosphite is rapidly completed at 50 °C.[15]

The introduction of electron-accepting substituents into the alkoxy-group of the trialkyl phosphite lowers its reactivity in the exchange reactions with PCl_3. The disproportionation of the chloro-substituted phosphites has been noted only on heating[20]. The exchange between tris(perfluoroalkyl) phosphites and PCl_3 is in general difficult[21]. The exchange between tris(trifluoroethyl) phosphites and PCl_3 at 90 °C reaches completion in 4 h:[22]

$$(CF_3CH_2O)_3P + PCl_3 \rightleftarrows (CF_3CH_2O)_2PCl + CF_3CH_2OPCl_2 .$$

Triaryl phosphites enter into exchange reactions with phosphorus trihalides with much more difficulty than trialkyl phosphites. The reactions of triphenyl phosphite with PCl_3

and PBr_3 take place on heating above 150 °C and mixtures of diphenyl phosphorohalidites and phenyl phosphorodihalidites are then formed[23,24]. According to NMR data, the half-exchange period at 160 °C in the reaction of triphenyl phosphite with PCl_3 is 15 h:[10]

$$(C_6H_5O)_3P + PCl_3 \rightarrow (C_6H_5O)_2PCl + C_6H_5OPCl_2 .$$

In the reaction between triphenyl phosphite and PCl_3 at 180 °C, equilibrium is established in 60 h between the initial reactants, diphenyl phosphorochloridite and phenyl phosphorodichloridite[24], but, on raising the temperature to 200° to 230 °C and using an excess of PCl_3, the triaryl phosphites can be fully converted into aryl phosphorodichloridites[25]:

$$(ArO)_3P + 2PCl_3 \rightleftarrows 3ArOPCl_2 ,$$
$$Ar = C_6H_5,\ p\text{-}CH_3C_6H_4,\ m\text{-}CH_3C_6H_4,$$
$$2,\ 4\text{-}(CH_3)_2C_6H_3 .$$

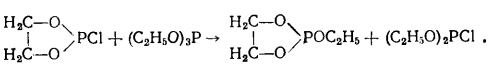
The nature of phosphorus halides exerts a significant influence on the direction and rate of the exchange reactions. Phosphorus trihalides undergo exchange reactions with trialkyl phosphites most vigorously and in terms of their reactivity can be arranged in the sequence[10] $PF_3 < PCl_3 < PBr_3$.

The interaction of trialkyl phosphites with phosphorus iodides leads to the formation of a complete mixture of products even under the conditions of intense cooling. The reactions of trialkyl phosphites with PBr_3 proceed exothermically and, like those with PCl_3, are completed by the formation of exchange products[10]:

$$2(C_3H_7O)_3P + PBr_3 \rightleftarrows 3\,(C_3H_7O)_2PBr .$$

The reactions between trialkyl phosphites and phosphorus trifluoride proceed with greater difficulty. The reaction between $(CH_3O)_3P$ and PF_3 is completed in 40 h at 80 °C but at a higher temperature it is complicated by the formation of phosphorus(V) derivatives[26].

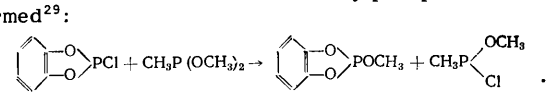
Trialkyl phosphites react with alkyl phosphorochloridites more slowly than PCl_3, but the reactions with ethylene phosphorochloridite and phenylene phosphorochloridite, like those with PCl_3, proceed with evolution of heat, which can be accounted for by the favourable conditions for the formation of the intermediate complex[27]:



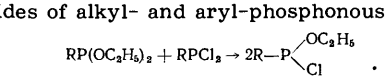
An increase of electron density at the phosphorus atom in phosphorus acid esters increases their reactivity in exchange reactions. Dialkyl phosphonites are more reactive than trialkyl phosphites; the interaction of dialkyl phosphonites with PCl_3 is exothermic and leads to the complete exchange of the alkoxy-groups and the formation of dichlorophosphines[28]:

$$RP(OR')_2 + PCl_3 \rightarrow RPCl_2 + (R'O)_2PCl .$$

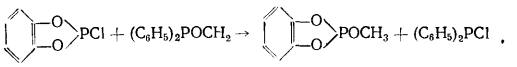
The analogous reaction with PBr_3 leads to a complex mixture of products[10]; the reaction with phosphorochloridites is slower and the ester-chlorides of alkylphosphonous acids are formed[29]:



The reactions of dialkyl phosphonites with dichlorophosphines can serve as a convenient method of synthesis of the ester-chlorides of alkyl- and aryl-phosphonous acids[30,31]:



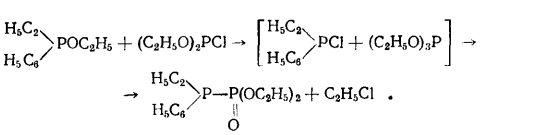
The esters of phosphinous acids react with phosphorus halides even more vigorously. The reactions of dialkyl phosphinites with PCl_3 give rise to a complex mixture of products[10,28], but the reaction with phenylene phosphorochloridite results in the formation of exchange products[29]:



Rapid exchange has also been observed in the reaction of butyl dibutylphosphinite with dipropyl phosphorochloridite[10]:

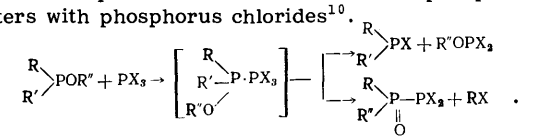
$$(C_4H_9)_2POC_4H_9 + (C_3H_7O)_2PCl \rightarrow (C_4H_9)_2PCl + (C_3H_7O)_2POC_4H_9 .$$

In the reaction of ethyl ethylphenylphosphinite with diethyl phosphorochloridite the products formed initially subsequently condense to form a P–P bond with alteration of the coordination number of one of the phosphorus atoms[32,33]:



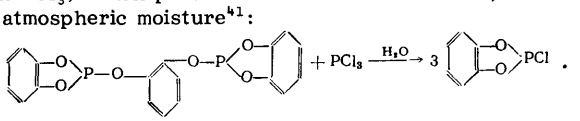
This competing reaction occurs in almost all cases when acid esters of tervalent phosphorus interact with phosphorus chlorides and, depending on the structure of the initial compounds and the exchange products, lead to the formation (in greater or smaller amounts) of side products containing a P–P bond. When trialkyl phosphites react with PCl_3, the exchange reaction is mainly observed and condensation products are formed in insignificant amounts[9]. However, in the reactions of trialkyl phosphites with certain chlorophosphines[29,33,34] and iodophosphines[35,36], the latter pathway becomes the main one, which can be used to synthesise compounds containing a P–P bond[35–40].

The formation of compounds with a P–P bond can be a result of an alternative pathway to the decomposition of the intermediate complex formed in the reaction of phosphorus acid esters with phosphorus chlorides[10].



The available information about the structure of the intermediate complex in the reactions of trialkyl phosphites with phosphorus chlorides is inadequate. The question of the mechanism of these exchange reactions is complicated by catalysis. Both acids and bases have a catalytic effect in reactions involving the exchange of alkoxy- and aryloxy-groups between tricoordinate phosphorus compounds. HCl is a powerful catalyst in the reactions of trialkyl phosphite with PCl_3 and it is extremely difficult to eliminate admixtures of this acid[10]. The acid esters of tervalent phosphorus, which can be formed when the neutral esters are acted upon by HCl or traces of H_2O, are also effective catalysts in these reactions[10]. Boron trichloride and triethylamine have likewise been found to be catalytically active in the exchange reactions of neutral phosphites with phosphorus chlorides[27]. It has been shown by ^{31}P NMR that exchange between tricoordinate phosphorus esters and chlorides catalysed by HCl is preceded by the formation of compounds with a P–P bond[32].

Catalysis can be observed even when the reaction mixture is insufficiently protected from atmospheric moisture. Thus it has been shown that the reaction of phenylene phosphite with PCl_3, which proceeds under mild conditions, is catalysed by atmospheric moisture[41]:



The disproportionation of phenyl phosphorodichloridite when the latter is stored for a month can be accounted for by the catalytic effect of HCl or traces of water[42]:

$$3C_6H_5OPCl_2 \rightarrow (C_6H_5O)_3P + 2PCl_3 .$$

The isotope exchange between phenyl phosphorodichloridite and the radioactive $^{32}PCl_3$ at 20 °C is apparently induced by the same factors[43]:

$$C_6H_5OPCl_2 + {}^{32}PCl_3 \rightleftarrows C_6H_5O^{32}PCl_2 + PCl_3 .$$

Nor can one rule out the phenomenon of autocatalysis in reactions involving the exchange of ester groups at the phosphorus atom. Thus aryl phosphorodi-iodites undergo symmetrisation to triaryl phosphites and phosphorus triiodide on storage, the symmetrisation reaction being accelerated by the addition of PI_3:[44]

$$3\,ArOPI_2 \rightarrow [(ArO)_3P + 2PI_3] \rightarrow (ArO)_3PI_2 + P_2I_4 ;$$
$$Ar = C_6H_5,\ o\text{-}CH_3C_6H_4,\ m\text{-}CH_3C_6H_4,$$
$$p\text{-}CH_3C_6H_4,\ o\text{-}ClC_6H_4,\ p\text{-}ClC_6H_4 .$$

Acids and bases can also catalyse the exchange of ester groups between neutral phosphites. In the presence of HCl the reaction between triethyl and trimethylphosphites takes place in 2 h at 20 °C with formation of mixed phosphites[45]

$$(C_2H_5O)_3P + (CH_3O)_3P \overset{HCl}{\rightleftarrows} (C_2H_5O)_2POCH_3 + (CH_3O)_2POC_2H_5 .$$

This reaction is apparently reversible because in the presence of acid reagents, for example, trifluoroacetic acid, rapid symmetrisation of the mixed neutral phosphites is observed at the same temperature[46]. It has been suggested that HCl protonates the oxygen of the alkoxy-group of the phosphite with its subsequent cleavage to dialkyl phosphorochloridite, which then interacts with another phosphite molecule to form the exchange products[32,45].

Under the condition of base catalysis, the exchange of ester groups between neutral phosphites proceeds under much more severe conditions. According to NMR data, the exchange between triethyl and tributyl phosphite is completed in 4 h at 170–180 °C:[47]

$$(C_2H_5O)_3P + (C_4H_9O)_3P \xrightarrow{C_4H_9ONa} (C_2H_5O)_2POC_4H_9 + (C_4H_9O)_2POC_2H_5 .$$

An interesting process involving the exchange of alkoxy-groups for aryloxy-groups has been observed in the presence of alkyl halides. The exchange is accompanied by the Arbuzov reaction, which results in the formation of mixed esters of alkylphosphonic acids[48,49].

The redistribution of ester groups with participation of trialkyl phosphites, triphenyl phosphite, and phosphorous acid takes place at 80–100 °C with formation of mixed acid esters of phosphorous acid[50]:

$$(C_6H_5O)_3P + (RO)_3P + H_3PO_3 \rightarrow 3\ \begin{matrix} RO \\ C_6H_5O \end{matrix}\!\!>\!P(O)H .$$

The marked acidophilic properties of both aliphatic and aromatic neutral esters of tervalent phosphorus promote their involvement in exchange reactions with various phosphorus acids. Neutral phosphites interact with phosphorous acid at 20 °C to form mixtures of acid phosphites[51]:

$$(RO)_3P + H_3PO_3 \rightarrow (RO)_2P(O)H + ROP(O)H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH \quad .$$

The composition of the products of this reaction depends on its conditions and on the ratio of the initial reactants. When a mixture of neutral phosphites and phosphorous acid taken in proportions of 2 : 1 is heated at 100 °C for 2 h, dialkyl or diaryl phosphites are formed as the main products[52–55]:

$$2\,(RO)_3P + H_3PO_3 \rightarrow 3\,(RO)_2P(O)H ;$$
$$R = CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9,\ C_5H_{11},\ C_6H_{13},$$
$$C_6H_5CH_2,\ C_6H_5,\ p\text{-}CH_3C_6H_4,\ o\text{-}CH_3C_6H_4,$$
$$m\text{-}CH_3C_6H_4,\ p\text{-}ClC_6H_4,\ o\text{-}ClC_6H_4 .$$

Under the same conditions, neutral phosphites interact also with acid phosphites, which can result in the formation of mixed acid phosphites. This reaction is particularly convenient for the synthesis of mixed acid phosphites containing alkoxy- and aryloxy-groups[50,56]:

$$(RO)_3P + R'OP\!<\!\begin{matrix}(O)H \\ OH\end{matrix} \rightarrow \begin{matrix} RO \\ R'O \end{matrix}\!\!>\!P(O)H + (RO)_2P(O)H .$$

The exchange reactions of triaryl phosphites with phosphorous acid are apparently reversible, because diaryl phosphites are symmetrised on slow vacuum distillation to triaryl phosphites. This process is accelerated in the presence of bases[57,58]:

$$3\,(C_6H_5O)_2P(O)H \rightarrow 2\,(C_6H_5O)_3P + H_3PO_3 .$$

Such symmetrisation is not characteristic of dialkyl phosphites, but sodium dialkyl phosphorothioites undergo symmetrisation on heating[59]:

$$2(RO)_2PSNa \rightarrow (RO)_3P + ROP(SNa)_2 .$$

When salts of dialkyl phosphites are heated, the products of the Arbuzov rearrangement are usually formed[60], but, when a mixture of di(s-butyl) phosphite was heated with its sodium salt, the exchange products were obtained, which was apparently caused by the steric hindrance to the Arbuzov rearrangement[61]:

$$(s\text{-}C_4H_9O)_2P(O)H + (s\text{-}C_4H_9O)_2PONa \rightarrow$$
$$\rightarrow (s\text{-}C_4H_9O)_3P + (s\text{-}C_4H_9O)P(O)H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad ONa \quad .$$

It is noteworthy that in the reactions of mixed neutral alkyl aryl phosphites with phosphorous acid, the alkoxy-group is more mobile[56]:

$$(C_2H_5O)_2POC_6H_5 + H_3PO_3 \rightarrow \begin{matrix} C_2H_5O \\ C_6H_5O \end{matrix}\!\!>\!P(O)H + C_2H_5OP(O)H .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

The reactions of neutral phosphites with phosphorous acid take place stepwise. The dialkyl phosphite formed initially interacts at a higher temperature with phosphorous acid to form monoalkyl phosphites[62,63]:

$$(RO)_2P(O)H + H_3PO_3 \rightarrow 2\,ROP(O)H .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

Neutral phosphites esterify phosphonous acids at 20 °C with formation of acid phosphonite esters[64]:

$$(RO)_3P + C_6H_5P(O)H \rightarrow (RO)_2P(O)H + C_6H_5P(O)H ;$$
$$\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\quad OH\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OR$$
$$R = CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9,\ iso\text{-}C_4H_9 .$$

Further esterification of phosphonous acid by neutral phosphites takes place at a higher temperature and is complicated by the rearrangement of the neutral phosphonite to the phosphinate[65]. Like phosphites, neutral phosphonites interact with phosphonous acids to form acid phosphonites[66,67]:

$$C_6H_5P(OR)_2 + C_6H_5P(O)H \rightarrow 2\,C_6H_5P(O)H ;$$
$$\qquad\qquad\qquad\quad |\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\quad OH\qquad\qquad\qquad\qquad\quad OR$$
$$R = C_6H_5,\ iso\text{-}C_8H_{17},\ ClCH_2CH_2 .$$

Alkoxy-groups can be exchanged also between acid phosphites. When a mixture of symmetrical dialkyl phosphites is heated for 15 h at 100–150 °C, asymmetric dialkyl phosphites

are formed in yields from 30 to 70%.[67,68] It has been demonstrated by gas–liquid chromatography (GLC) that the exchange takes place even at 24 °C:[69]

$$(RO)_2P(O)H + (R'O)_2P(O)H \rightleftarrows 2\ \begin{matrix} RO \\ R'O \end{matrix}\!\!>\!P(O)H\ ;$$

$R = CH_3,\ C_2H_5;\ R' = C_2H_5,\ C_3H_7,\ C_4H_9$
$C_5H_{11},\ C_6H_{13},\ C_8H_{17},\ ClCH_2CH_2,$
$(ClCH_2)_2CH$.

This reaction is reversible and mixed dialkyl phosphites are gradually symmetrised during storage[70,71]. The symmetrisation is accelerated on distillation[72] and in the presence of bases[70]. Alkylene diphosphites are symmetrised on heating[73]:

$$\begin{matrix} RO \\ H(O) \end{matrix}\!\!>\!POR'OP\!<\!\begin{matrix} OR \\ (O)H \end{matrix} \rightarrow R'\!<\!\begin{matrix} O \\ O \end{matrix}\!\!>\!P(O)H + (RO)_2P(O)H\ .$$

Under the influence of the full esters of tervalent phosphorus acids, the acids of quinquevalent phosphorus are also readily esterified. Thus triethyl phosphite is cleaved by phosphoric acid with the simultaneous formation of monoethyl phosphate[73,74]:

$$(C_2H_5O)_3P + H_3PO_4 \rightarrow (C_2H_5O)_2P(O)H + C_2H_5O\overset{O}{\overset{\|}{P}}(OH)_2\ .$$

The esterification of phosphoric acid by trialkyl phosphites takes place stepwise. Depending on the ratio of the initial reactants, mono-, di-, and tri-alkyl phosphates can be formed on heating in nitromethane[75,76]. The reaction of triphenyl phosphite with phosphoric acid also takes place stepwise under the same conditions:[77,78]

$$(RO)_3P + H_3PO_4 \left|\begin{array}{l} \xrightarrow{1:1} ROP(O)(OH)_2 + (RO)_2P(O)H \\ \xrightarrow{2:1} (RO)_2P(O)OH + 2(RO)_3P(O)H \\ \xrightarrow{3:1} (RO)_3PO + 3\,(RO)_2P(O)H\ . \end{array}\right.$$

The esterification of phosphoric acid by neutral phosphites is a complex process. The study of the mechanism of the esterification of diethyl phosphate showed that the process involves a stage in which the neutral phosphate is protonated and a mixed anhydride is formed[79]:

$$(RO)_3P + (C_2H_5O)_2P(O)OH \left|\begin{array}{l} \rightleftarrows (RO)_3\overset{+}{P}H\overline{O}P(O)(OC_2H_5)_2 \\ \rightleftarrows (RO)_3P{-}\overset{\uparrow\downarrow}{O}{-}P(O)(OC_2H_5)_2 \\ \quad\ \ H \\ \rightleftarrows (RO)_2P(O)P(O)(OC_2H_5)_2 + ROH \end{array}\right. \rightarrow$$

$$\rightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}OR + (RO)_2PHO\ .$$

The reactions of neutral phosphites with phosphonic acids apparently proceed in accordance with an analogous mechanism and here too neutral acid phosphonates can be obtained depending on the reactant ratio[80]:

$$(C_2H_5O)_3P + C_6H_5CH_2\overset{O}{\overset{\|}{P}}(OH)_2 \left|\begin{array}{l} \xrightarrow{1:1} C_6H_5CH_2\overset{O}{\overset{\|}{P}}\!<\!\begin{matrix} OC_2H_5 \\ OH \end{matrix} + (C_2H_5O)_2P(O)H \\ \xrightarrow{2:1} C_6H_5CH_2\overset{O}{\overset{\|}{P}}(OC_2H_5)_2 + 2(C_2H_5O)_2P(O)H\ . \end{array}\right.$$

The thioacids of quinquevalent phosphorus are readily esterified by the full esters of tervalent phosphorus acids. The reactions of trialkyl phosphites, dialkyl phosphonites, or alkyl phosphinites with dialkyl phosphorodithioates take place with evolution of much heat and trialkyl phosphorodithioates are formed. It has been suggested that the protonation of the tricoordinate phosphorus is an intermediate stage[81,82]:

$$R\!<\!\begin{matrix} R' \\ POR'' \end{matrix} + (R'''O)_2\overset{S}{\overset{\|}{P}}SH \rightarrow \left[R'\!\!-\!\overset{+}{P}H\overset{-}{S}\overset{S}{\overset{\|}{P}}(OR''')_2\right] \rightarrow (R'''O)_2\overset{S}{\overset{\|}{P}}SR'' + R'\!<\!\begin{matrix} R \\ P(O)H \end{matrix}\ .$$

Neutral phosphites and phosphonites react less vigorously with the acid esters of phosphoromonothioic acids. The esterification of *O,O*-dialkylphosphoromonothioic acid by trialkyl phosphites proceeds with evolution of a small amount of heat and is completed by the formation of thiono-isomers[81]:

$$(R'O)_2PR + (R''O)_2POSH \rightarrow (R''O)_2\overset{S}{\overset{\|}{P}}OR' + R'O\!<\!\begin{matrix} R \\ P(O)H \end{matrix}\ .$$

We may note that the analogous reaction of triphenyl phosphite with diethylphosphorothioic acid stops at the stage involving the formation of the mixed anhydride[83]:

$$(C_6H_5O)_3P + (C_2H_5O)_2POSH \rightarrow (C_6H_5O)_3POP\overset{S}{\overset{\|}{(}}OC_2H_5)_2 + C_6H_5OH\ .$$

Neutral esters of tricoordinate phosphorus acids also esterify phosphonodithioic acids and the completion of the reaction then requires heating for 1 h at 40–50 °C:[84]

$$(CH_3O)_3P + C_6H_5CH_2\overset{S}{\overset{\|}{P}}\!<\!\begin{matrix} OC_4H_9 \\ SH \end{matrix} \rightarrow C_6H_5CH_2\overset{S}{\overset{\|}{P}}\!<\!\begin{matrix} OC_4H_9 \\ SCH_3 \end{matrix} + (CH_3O)_2P(O)H\ .$$

The esters of quinquevalent phosphorus acids are much more inert in the exchange reactions, which can be explained by their coordination unsaturation, which hinders the formation of the intermediate reaction complex from the exchanging reactants. A competing pathway involving the formation of pyrophosphates occurs preferentially in the reactions of esters of phosphorus(V) acids with phosphorochloridites[85–88]. Pyrophosphoryl compounds are formed preferentially also in the reactions of neutral phosphates with phosphoramidochloridates[89–91], phosphorochlorothioates[92], thiophosphoryl trichloride[93], and phosphorus pentoxide[94]. Only the reaction of phosphorus trichloride with the chloroalkyl esters of phosphonic acids, which may be formed when aldehydes interact with PCl_3 in accordance with the scheme

$$3RCHO + PCl_3 \rightarrow [(RCHClO)_3P \rightarrow RCHClO\overset{O}{\overset{\|}{P}}(OCHClR)_2] \xrightarrow{PCl_3} RCHClO\overset{O}{\overset{\|}{P}}Cl_2\ ,$$

is an exception[95–97].

In contrast to triaryl phosphates[99], trialkyl phosphates[98] undergo the exchange reaction with phosphoric acid, which is catalysed by stronger acids[98]:

$$2(RO)_3PO + H_3PO_4 \rightarrow 3\,(RO)_2P(O)OH\ .$$

Acid catalysis can also explain the incorporation of the radioactive ^{32}P label into neutral phosphates on interaction with labelled iron phosphate[100]:

$$(RO)_3PO + Fe^{32}PO_4 \cdot 2H_2O \xrightarrow{200°C} (RO)_3{}^{32}PO\ .$$

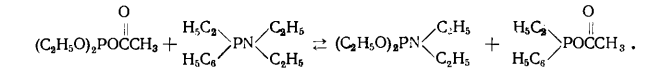
The incorporation of radioactive phosphorus has been observed also on heating tributyl phosphate with radioactive phosphoric acid[101]:

$$2\,(C_4H_9O)_3PO + H_3{}^{32}PO_4 \rightleftarrows (C_4H_9O)_3{}^{32}PO + \\ + (C_4H_9O)_2\overset{O}{\overset{\|}{P}}OH + C_4H_9O\overset{O}{\overset{\|}{P}}(OH)_2\ .$$

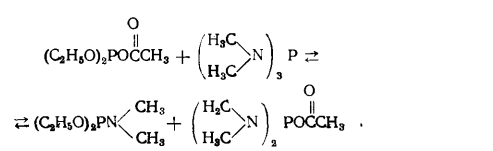
It is noteworthy that the enzyme-catalysed exchange reactions of monophosphates with radioactive phosphoric acid are faster and proceed under milder conditions[102].

2. The Exchange of Acyloxy-Groups

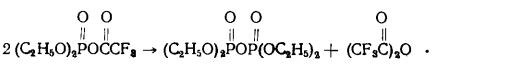
O-Acyl derivatives of phosphorus acids constitute a broad class of mixed anhydrides. Among them, acylphosphites have been studied in greatest detail (the bibliography includes more than 100 items[103]). It has been shown by ^{31}P NMR that, when acetyl diethyl phosphite is heated with the diethylamide of ethylphenylphosphinous acid at 50 °C, a mobile equilibrium is established between these compounds and the exchange products[104]:



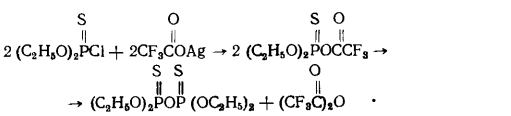
When these reagents are heated at a higher temperature, diphosphine oxide and acetic anhydride are formed. Their formation is most probably associated with the symmetrisation and isomerisation reactions of the mixed anhydrides. There are no data in the literature on the symmetrisation of acyl phosphites, but the formation of pyrophosphites when dialkyl phosphites interact with isocyanates can serve as direct confirmation of the possibility of the occurrence of such reactions[105]. The formation of pyrophosphorous acid derivatives has been observed also in the reactions of acyl phosphites with phosphorous acid triamides[14,106]. It was shown by NMR that under these conditions the formation of pyrophosphoryl compounds is preceded by the exchange of the acyloxy-group between the phosphorus compounds[104]:



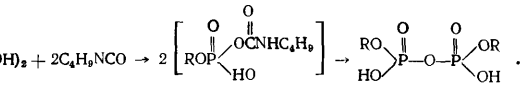
O-Acyl derivatives of phosphorus(V) acids readily undergo symmetrisation as a consequence of their high reactivity. Thus the mixed anhydride of *O*,*O*-diethylphosphoric and trifluoroacetic acids is wholly converted into tetraethyl pyrophosphate and trifluoroacetic acid anhydride after 24 h at 20 °C:[107]



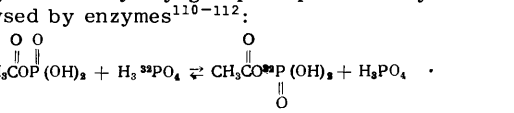
Ethoxycarbonyl diethyl phosphate, which persists for several months, is very stable[107]. The tendency towards analogous reactions has been noted also for *O*-acyl derivatives of phosphoromonothioic acid[108]:



The tendency of the acyloxy-derivatives of phosphorus towards symmetrisation can be used to synthesise pyrophosphoryl compounds which are difficult to obtain. Thus disubstituted pyrophosphates have been prepared by the interaction of phosphoric acid monoesters with butyl isocyanate[109]:

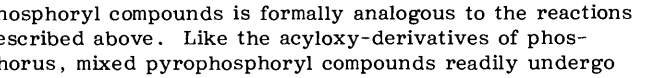


The exchange of the acyloxy-groups is promoted by acids and is catalysed by enzymes[110–112]:

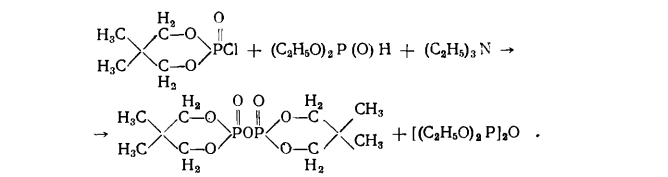


3. The Exchange of Phosphorus-Containing Groups

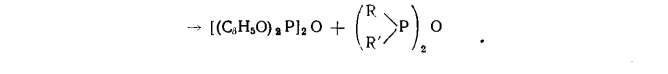
The exchange of phosphorus-containing groups in pyrophosphoryl compounds is formally analogous to the reactions described above. Like the acyloxy-derivatives of phosphorus, mixed pyrophosphoryl compounds readily undergo symmetrisation. In many instances symmetrisation takes place even during the preparation of the mixed anhydrides, for example, the anhydride of *O*,*O*-diethylphosphoric and *O*,*O*-diethylphosphorous acids[113–115]:



Only the symmetrical anhydrides have been obtained in the reaction of diethyl phosphite with dimethyl propylene phosphorochloridate[115]:

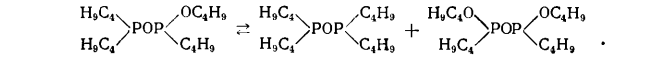


The interaction of acid phosphites[116,117] and phosphonites[118] as well as phosphinous acids[119,120] with the chlorides of tervalent phosphorus acid in the absence of hydrogen chloride acceptors leads to the exchange of the hydroxy-group for chlorine and, in the presence of bases, results in the formation of mixed anhydrides, which then undergo symmetrisation[121–123]:

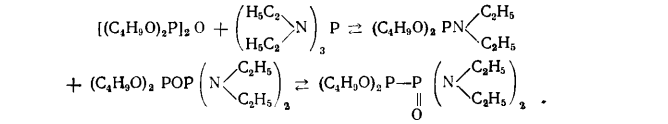


Symmetrical phosphorus acid anhydrides can be obtained also directly by treating the mixed anhydrides of phosphorus acids with the acids themselves[124,125].

We may note that the symmetrisation of the mixed anhydrides of phosphinous and *O*-alkylphosphinous acids is reversible[123]:



The interaction of tetrabutyl pyrophosphite with phosphorous acid tris(diethylamide) leads to the formation of the diethylamide of *O*,*O*-dibutylphosphorous acid and dibutyl *N*,*N*,*N*′,*N*′-tetraethylpyrophosphorodiamidite, which is in tautomeric equilibrium with diphosphine monoxide[126]:



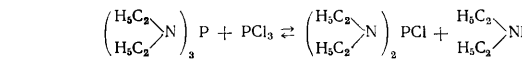
This reaction is of interest also because the exchange of the phosphorus-containing groups proceeds with the cleavage of not only the P–O but also the P–P bonds[127]. Instances of the tautomeric transformation of diphosphine oxides into anhydrides have been examined[128]. A similar preliminary isomerisation has also been postulated in the exchange reaction of diphosphine disulphides with phosphorus-acid chlorides[129]. However, the exchange involving the P–P bond can proceed also without the preliminary isomerisation of diphosphine oxides. Thus dialkyld'phenoxydiphosphine and

dialkyl phosphorochloridite have been obtained by the reaction of diphenyl phosphorochloridite with dialkoxydialkyldiphosphine[129].

The exchange reactions involving the cleavage of the P–P bond have been examined in reviews[131,132].

4. The Exchange of Amino-Groups

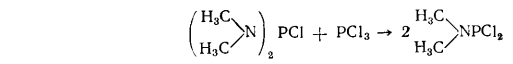
Phosphorus acid amides are more reactive in exchange reactions than their esters. The reaction of phosphorous tris(diethylamide) with PCl_3 takes place almost instantaneously with evolution of much heat and is accompanied by the redistribution of the substituents[9]:



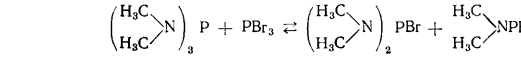
By altering the ratio of the initial reactants, the reaction can be directed towards the preferential formation of phosphorodiamidous chlorides[133–136]:

$$2\,(R_2N)_3\,P + PCl_3 \rightleftarrows 3\,(R_2N)_2\,PCl\,;\quad R=CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9\,.$$

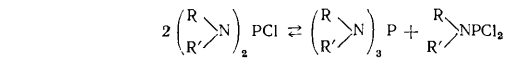
The half-life of this reaction at 20 °C is 30 s.[137] The *N,N,N',N'*-tetra-alkylphosphorodiamidous chlorides formed react in their turn with PCl_3 to produce *N,N*-dialkylphosphoramidous dichlorides[138]:



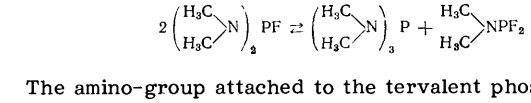
Phosphorus triamides react extremely vigorously also with PBr_3, but the *N,N,N',N'*-tetra-alkylphosphorodiamidous bromides formed are unstable and disproportionate to the initial compounds even on vacuum distillation[134]:



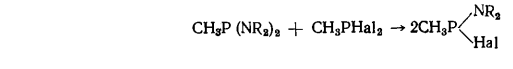
N,N,N',N'-Tetra-alkylphosphorodiamidous chlorides, which disproportionate to the extent of 15% with formation of phosphorous triamides and phosphoramidous dichlorides after storage for 1 month at 20 °C, are also relatively unstable[139]:



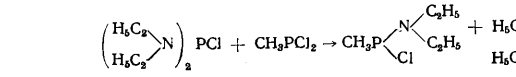
N,N,N',N'-Tetra-alkylphosphorodiamidous fluorides disproportionate even faster and for this reason it is difficult to isolate them in a pure form[140]:



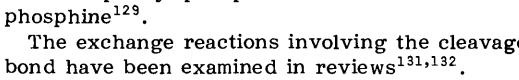
The amino-group attached to the tervalent phosphorus atom is readily exchanged in the reactions of a wide variety of OPC with phosphorus chlorides[27,137,141,142]. The reactions of bis(dialkylamino)phosphorines with dichloro- and dibromophosphines take place at high rates[137,142]:



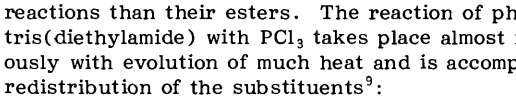
N,N,N',N'-Tetra-alkylphosphorodiamidous chlorides react with alkyldichlorophosphines under mild conditions[137]:



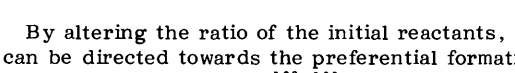
The exchange between phosphorous triamide and diethyl phosphorochloridodithioite is rapid[141]:



The *N,N,N',N'*-tetra-alkylphosphorodiamidous chloride formed in this reaction reacts under the same conditions with the excess of diethyl phosphorochloridodithioite and *N,N*-diethylphosphoramidous dichloride is formed[141]:

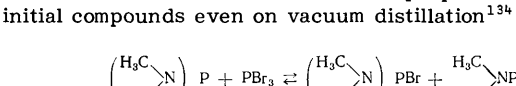


N,N-Diethylphosphoramidous dichloride can also be obtained by the reaction of phosphorous tris(diethylamide) with ethyl phosphorodichloridothioite[141]:

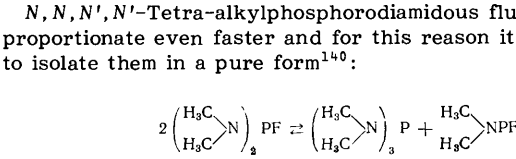


The exchange of the amino-group for chlorine is also observed in the interaction of the ester-amides of phosphorous acid with phosphorochloridites. Ethylene *N,N*-diethylphosphoramidite and diethyl phosphorochloridite have been obtained by the reaction of diethyl *N,N*-diethylphosphoramidite with ethylene phosphorochloridite, which takes place with spontaneous heating[27]:

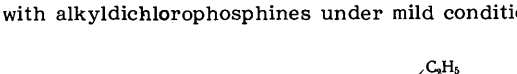
Diethyl *N,N*-diethylphosphoramidite interacts less vigorously with phenylene phosphorochloridite. The catalytic effect of HCl was noted in this reaction[27]:



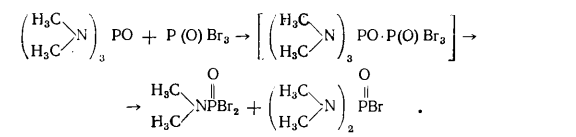
The exchange of a nitrogen-containing functional group in phosphoramidites and phosphonamidites for chlorine goes to completion and the formation of only a small amount of red condensed products, tentatively assumed to be monomers with a P–P bond, is observed[136]. However, the final product of the reaction of ethylphenylphosphinous diethylamide with diethyl phosphorochloridite is a compound with a P–P bond, which is formed after the completion of the exchange reaction[27]:



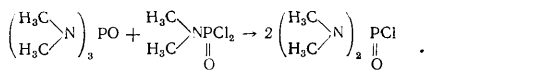
The amides of phosphorus(V) acids enter into exchange reactions with phosphorus chloride under more severe conditions than the analogous derivatives of tervalent phosphorus. Phosphoric triamides react with $POCl_3$ to form stable complexes which withstand heating to 150 °C. At a higher temperature they decompose with formation of phosphoromonoamidic dichloride and phosphorodiamidic chloride, i.e. an exchange reaction takes place[143,144]:



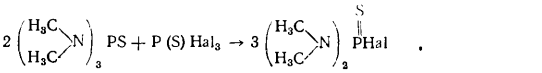
Phosphoryl bromide reacts similarly[144]:



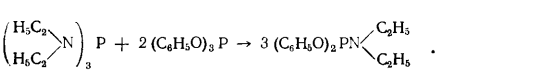
Phosphoric tris(dimethylamide) reacts with *N*,*N*-dimethylphosphoramidic chloride[144]:



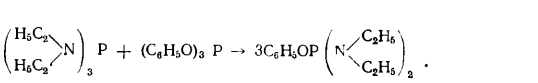
It is noteworthy that the thioamides of phosphorus acids undergo the exchange reaction under milder conditions. Phosphorothioic tris(dimethylamide) reacts with $PSCl_3$ and $PSBr_3$ on refluxing in toluene. The formation of a complex was not observed in these reactions and *N*,*N*,*N*',*N*'-tetramethylphosphorodiamidothioic halides were obtained in high yields[144]:



Instead of exchange products, pyrophosphoryl compounds and an alkyl halide are formed in the reactions of phosphorus(V) acid chlorides with the ester-amides of the same acids containing at least one alkoxy-group at the phosphorus atom[89-92]. However, in the series of aryloxyamides there is a possibility of the exchange of the amino-groups for chlorine and even for an aryloxy-group. When a mixture of phosphorous tris(diethylamide) is heated with triphenyl phosphite for 5 days at 100 °C, complete exchange takes place with formation of diphenyl *N*,*N*-diethylphosphoramidite in 93% yield[9,145]:

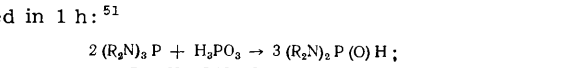


In the presence of an excess of phosphorous tris(diethylamide), phenyl *N*,*N*,*N*',*N*'-tetra-alkylphosphorodiamidite was obtained under the same conditions[146]:

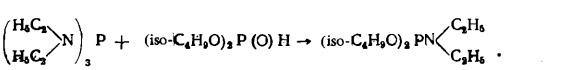


The occurrence of this reaction shows that diaryl phosphoramidites can undergo a reaction involving a redistribution of the amido- and aryloxy-groups at 100 °C and above[145].

The presence of the nitrogen atom in phosphorus acid amides promotes the formation of complexes with proton-donating reagents[27,147-149] and hence the occurrence of exchange reactions between phosphorus acids and their amides. The exchange between phosphorous triamides and phosphorous acid is observed even at 20 °C and at 60 °C is completed in 1 h:[51]

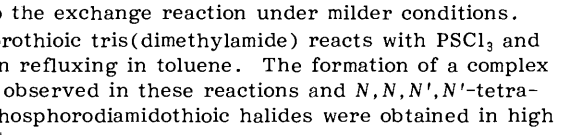


Although the yields of this reaction are approximately 60%, it nevertheless constitutes the most convenient method of synthesis of phosphoramidites[150,151]. On heating for 6 h at 100 °C, the exchange between phosphorous tris(diethylamide) and di-isobutyl phosphite is observed[152]:



The analogous reaction of butyl *N*,*N*,*N*',*N*'-tetraethylphosphorodiamidite with an acid phosphite stops at the stage involving the formation of a mixed anhydride[152]:

The interaction of tervalent phosphorus acid amides with quinquevalent phosphorus acids is more complex. Together with exchange reactions, pyrophosphoryl compounds are formed and a free amine is liberated in this instance[148]; by removing the amine from the reaction mass, it is possible to drive the reaction fully towards the formation of pyrophosphates and their thio-analogues[153-155]:

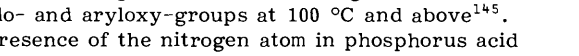


The reactions of phosphorus(V) acids with their amides stop at the stage involving the formation of only pyrophosphoryl compounds and ammonium salts of phosphorus acids[156,157], which is apparently associated with the high stability of these salts. In this connection it is of interest to note that, when phosphoric acid triamides react with carboxylic acid salts, an amino-group is exchanged for a hydroxy-group[158].

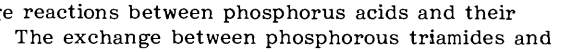
5. The Exchange of Alkylthio- and Arylthio-Groups

As regards their chemical properties, phosphorus acid thioesters differ significantly from their oxygen analogues. The thioesters show a smaller tendency towards being protonated, but their molecules are more polarisable. The sulphur atom in the thioesters of phosphorus(III) acids is capable of competing effectively with the phosphorus atom in reactions with electrophiles[159]. The thiophosphoryl group dissociates more readily than the phosphoryl group. These features have a significant influence on reactions involving phosphorus acid thioesters.

The reaction of trialkyl phosphorotrithioites with PCl_3 proceeds without the liberation of heat, but its completion requires heating[160]:

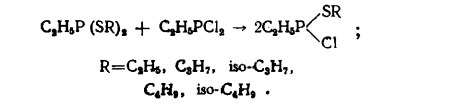


Since the equilibrium in this reaction is established slowly, the exchange products can be separated by vacuum distillation, which makes it possible to use the reaction for the synthesis of dialkyl phosphorochloridodithioites. Thus diethyl phosphorochloridodithioite has been obtained in 74% yield by heating a mixture of triethyl phosphorothioite with a stoichiometric amount of PCl_3 at 110–130 °C for 4 h:[141]

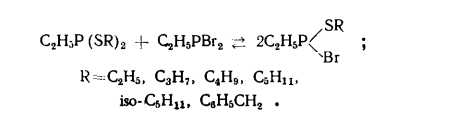


Diethyl phosphorobromidodithioite has been obtained in 70% yield under the same conditions by the reaction of triethylphosphorotrithioite with PBr_3.[141]

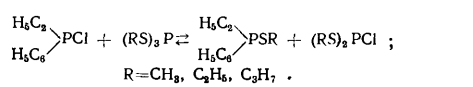
With increase of electron density at the phosphorus atom in the thioesters, the exchange of thiol groups is accelerated. The reactions of alkyl phosphonodithioites with dichlorophosphines are completed in 1 h at 100 °C and constitute a convenient method of synthesising the ester-chlorides of alkylphosphonothious acids[161,162]:



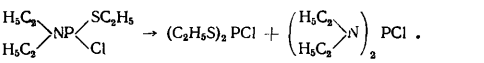
However, with increase of electron density at the phosphorus atom, the mobility of the equilibrium also increases, which can hinder the isolation of the reaction products by distillation. The yield of the ester-bromides obtained by the reaction of the full esters of alkylphosphonodithious acids with alkyldibromophosphines is only 30–60%:[163,164]



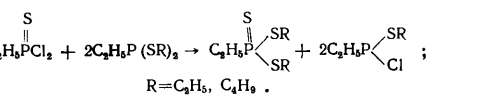
The equilibrium involving chlorophosphines is even more mobile. The reaction of chloroethylphenylphosphine with trialkylphosphorotrithioites is fully reversible and the attempts to isolate the exchange products by vacuum distillations were therefore unsuccessful[141]:



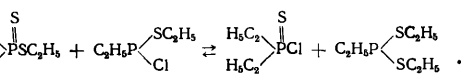
A mobile equilibrium is also established in the interaction of ethyl phosphorodichloridothioite with phosphoramidites; according to NMR data, the reaction of ethyl phosphorodichloridothioite with phosphorous tris(diethylamide) results in the formation of ethyl *N,N*-diethylphosphoramidochloridothioite, but vacuum distillation led to the isolation of only its disproportionation products[141]:



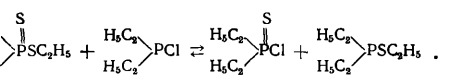
The exchange of alkylthio-groups is observed also in the reactions of dialkyl ethylphosphonodithioites with ethylphosphonothioic dichloride[165]:



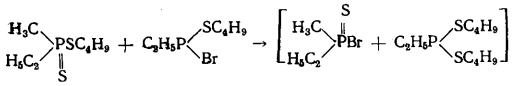
In contrast to their oxygen analogues, the thioesters of phosphorus(V) acids can enter into an exchange interaction with phosphorus halides. The exchange of the thiol group for a halogen then proceeds smoothly only in sulphur-containing compounds without an oxygen atom attached to the phosphorus atom. The exchange between phosphinodithioates and phosphorus chlorides proceeds under the mildest conditions. In a mixture of ethyl diethylphosphinodithioate and the ester-chloride of ethylphosphonothioic acid, the exchange is completed in 3 h at 100 °C. However, the exchange products have been isolated in a low yield apparently owing to the high mobility of the equilibrium[166]:



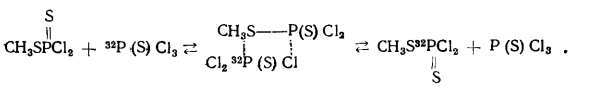
An analogous reaction with chlorodiethylphosphine has been observed on heating in a sealed tube at 140 °C, but the separation of the exchange products by distillation proved to be difficult[167]:



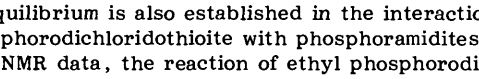
When butyl ethylmethylphosphinodithioate was allowed to react with butyl ethylphosphonobromidothioite, only dibutyl ethylphosphonotrithioate was isolated (in a low yield)[168]:



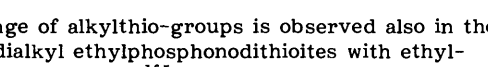
The thiol groups are exchanged for chlorine under more severe conditions in the interaction between the esters and chlorides of phosphorothioic and phosphonothioic acids. The isotope exchange between methyl phosphorodichloridodithioate and $^{32}PSCl_2$ proceeds at an appreciable rate on heating to a temperature above 150 °C and at 200 °C is 50% complete after 5 h. The isotope exchange takes place as a result of the exchange of the methylthio-group for Cl and apparently involves an associative mechanism[43]:



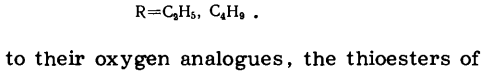
Phosphorotetrathioates react with $PSCl_3$ under the same conditions. Dialkyl phosphorochloridotrithioates have been obtained in 60–70% yield from trialkyl phosphorotetrathioates after 4 h at 180–200 °C:[169]



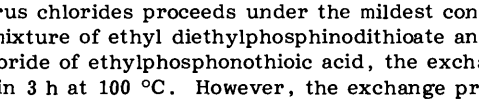
This reaction always results in the formation also of small amounts of alkyl phosphorodichloridodithioates, which become the main reaction products when an excess of thiophosphoryl chloride is used. Triphenyl phosphorotetrathioate has been converted into phenyl phosphorodichloridodithioate by an analogous procedure[169–171]:



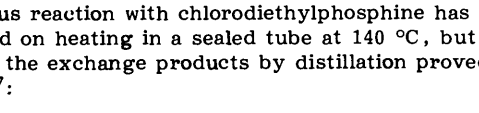
Dialkyl phosphorochloridotrithioates react with $PSCl_3$ under the same conditions to form phosphorodichloridodithioates[170]:



Like the phosphorotetrathioates, phosphonotrithioates react with alkyl- or aryl-phosphonothioic dichlorides, but the completion of the reaction requires in this case heating for ~12 h at 180–200 °C:[172]



Thioesters of phosphorus acids containing an oxygen atom attached to the phosphorus atom form as a rule pyrophosphoryl compounds and not exchange products in the reaction with phosphorus chlorides. The exchange products have been obtained only from certain phosphorodichloridothioates and $PSCl_3$:[173–176]



The thioesters of phosphorus acids also enter into a reaction with thioanhydrides in which the thiol groups are redistributed. When a mixture of phosphorotetrathioates is

heated with P_4S_{10} at 150 °C, an equilibrium is established between the initial compounds and the redistribution products[177]:

$$2\,(RS)_3PS + P_4S_{10} \rightleftarrows 3\,(RSPS_2)_2 .$$

A redistribution of alkylthio-groups is observed also in the interaction between unlike trialkyl phosphorotrithioites, the reaction being accelerated by HCl. Heating of a mixture of trimethyl and tributyl phosphorotrithioites in the presence of traces of HCl leads to rapid exchange of the alkylthio-groups[160]:

$$(CH_3S)_3P + (C_4H_9S)_3P \xrightarrow{HCl} (CH_3S)_2PSC_4H_9 + (C_4H_9S)_2PSCH_3 .$$

However, phosphorotrithioites and phosphonodithioites are not quite so highly acidophilic as their oxygen analogues and instances of the exchange of thiol groups between phosphorus thioesters and acids have not been described in the literature. It is only known that the acid phosphorus thioesters readily disproportionate. Thus *S,S*-dialkyl phosphorodithioites disproportionate even at room temperature or on slight heating into trialkyl phosphorotrithioites and *S*-alkyl phosphorothioites[178-180]:

$$2\,(RS)_2P(O)H \rightleftarrows (RS)_3P + RSP\begin{matrix}(O)H\\ OH\end{matrix} .$$

The monothiol esters of phosphorus acids are unstable in a free state and decompose with liberation of a thiol and phosphorus compounds[181,182].

6. The Exchange of Hydrocarbon Groups

The phosphorus–carbon bond is very strong. Until recently, it was believed that reactions accompanied by the cleavage of the P–C bond are rather anomalous in phosphorus chemistry[183] and that radioactive phosphorus attached to a carbon atom is not involved in isotope exchange[6]. However, careful studies have been carried out recently on a series of OPC with a P–C bond and resulted in the discovery of a number of new reactions involving the cleavage of the P–C bond[43,184-190] and indicating the possibility of the exchange of organic substituents between phosphorus compounds.

The conversion of dichlorophenylphosphine into chlorodiphenylphosphine has been known since the previous century[191]:

$$2\,C_6H_5PCl_2 \rightleftarrows \begin{matrix}H_5C_6\\ H_5C_6\end{matrix}\!\!>\!PCl + PCl_3 .$$

In the absence of a catalyst, this reaction takes place at 300 °C under pressure[191] or on pyrolysis in a quartz tube[192]. Under the catalytic influence of $AlCl_3$, the reaction is completed faster at a lower temperature and in the absence of pressure[193]. Zinc chloride, tin tetrachloride, slightly moistened $AlCl_3$, and other transition metal chlorides have also been proposed as catalysts of the symmetrisation of aryldichlorophosphines to diarylchlorophosphines[194-196]:

$$2ArPCl_2 \xrightarrow{AlCl_3} Ar_2PCl + PCl_3 ;$$
$$Ar = C_6H_5,\ o\text{-}ClC_6H_4,\ n\text{-}ClC_6H_4 .$$

We may note that benzyldihalogenophosphines disproportionate to dibenzylhalogenophosphines more specifically in the absence of catalysts and that this process is apparently reversible, since the removal of phosphorus trihalide from the reaction sphere is accompanied by an increase of the yield of the dibenzylhalogenophosphine[197]:

$$2C_6H_5CH_2PHal_2 \rightarrow (C_6H_5CH_2)_2PHal + PHal_3 .$$

It was found that $AlCl_3$ catalyses also the reverse reaction involving the redistribution of phenyl groups between the phosphorus compounds; thus ethylenebisdichlorophosphine has been obtained by the reaction of ethylenebisdiphenylphosphine with PCl_3 in the presence of $AlCl_3$ in a closed system at 280 °C:[198]

$$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 + 2PCl_3 \xrightarrow{AlCl_3} Cl_2PCH_2CH_2PCl_2 .$$

The interaction of phosphines with phosphorus chlorides is a complex process. In the initial stage of the reaction, the C–P bond is not involved and adducts are formed which undergo various reactions depending on the conditions. In the reactions of tertiary phosphines with phosphorus(V) chlorides under mild conditions, dichlorophosphoranes and polymeric products are formed[199-203]; on further heating to 180–200 °C, the initial tertiary phosphines and phosphorus chlorides are reformed[204,205]. Heating of the same reactants at still higher temperatures (220–260 °C) is accompanied by the cleavage of the C–P bond and the exchange of the hydrocarbon groups for Cl:[206]

$$(C_4H_9)_3P + PCl_3 \rightarrow (C_4H_9)_2PCl + C_4H_9PCl_2 .$$

The complete conversion of trialkylphosphines into alkyldichlorophosphines requires heating to 280–350 °C and the use of an excess of PCl_3:[206]

$$(C_4H_9)_3P + 2PCl_3 \rightarrow 3C_4H_9PCl_2 .$$

Tertiary phosphines interact with PBr_3 under similar conditions, which leads to the formation of dibromophosphines[207]:

$$(C_6H_5)_3P + 2PBr_3 \rightarrow 3C_6H_5PBr_2 .$$

The interaction of primary and secondary phosphines with PCl_3 under conditions where the mixture is cooled or slightly heated also does not involve the phosphorus–carbon bond[208-210], but at a higher temperature (~200 °C and above) the phosphorus–carbon bond is ruptured. This has been confirmed by the isotope exchange between alkyl- or aryldichlorophosphines and $^{32}PCl_3$ at 200–250 °C:[43,211]

$$RPCl_2 + {}^{32}PCl_3 \rightleftarrows R^{32}PCl_2 + PCl_3 .$$

The reaction is bimolecular, which indicates an associative mechanism, and proceeds at a fairly high rate; at 250 °C the degree of exchange reaches 50% after 5 h.

Isotope exchange has been observed also for phosphonothioic dichlorides[211]:

$$C_6H_5CH_2\overset{\overset{S}{\|}}{P}Cl_2 + {}^{32}PCl_3 \rightleftarrows C_6H_5CH_2{}^{32}\overset{\overset{S}{\|}}{P}Cl_2 + PCl_3 .$$

It is noteworthy that phosphonothioic dichlorides are involved in isotope exchange also with the radioactive $^{32}PSCl_3$ under the same conditions[211]:

$$C_6H_5CH_2\overset{\overset{S}{\|}}{P}Cl_2 + {}^{32}P(S)Cl_3 \rightarrow C_6H_5CH_2{}^{32}\overset{\overset{S}{\|}}{P}Cl_2 + P(S)Cl_3 .$$

The oxygen analogues do not enter into a similar reaction apparently because the formation of an intermediate complex is difficult for compounds of tetracoordinate phosphorus. The exception, which is observed for phosphonothioic dichlorides, can be accounted for by the fact that on heating they are capable of dissociating into sulphur and tricoordinate dichlorophosphines, which readily enter into an exchange reaction with PCl_3 or $PSCl_3$. This reaction constitutes a convenient method for the introduction of the radioactive ^{32}P label into pesticidal OPC.[212]

The exchange of hydrocarbon groups with phosphoryl chloride is also not observed in the series of oxygen-containing compounds of tetracoordinate phosphorus. Tertiary

phosphine oxides react with $POCl_3$ to form salt-like adducts which dissociate into the initial reactants on heating above the melting point and undergo pyrolytic decomposition[213–216]. The exchange of phenyl groups for Cl has also not been observed in the reaction of triphenylphosphine oxide with PCl_5, but this reaction was carried out under comparatively mild conditions[217–219].

The presence of a hydroxy-group in the hydrocarbon substituent in the α-position relative to the phosphorus atom increases significantly the lability of the phosphorus–carbon bond[185,220]. The exchange reactions involving a series of substituted OPC can also be facilitated in this way. Indeed tetra(hydroxymethyl)phosphonium hydroxide reacts with PH_3 under mild conditions to form tri(hydroxymethyl)phosphine[221]:

$$3\,(HOCH_2)_4\overset{+}{P}\overline{OH} + H_3P \rightarrow 4\,(HOCH_2)_3P + 3H_2O\ .$$

The high reactivity of the hydroxymethyl derivatives of phosphorus is also manifested in the exchange reactions of hydroxymethylphosphonium salts with tertiary phosphines, which results in the transfer of the hydroxymethyl group from the less nucleophilic to the more nucleophilic phosphorus centre[192–195]:

$$(HOCH_2)_4\overset{+}{P}\overline{Cl} + (C_4H_9)_3P \rightarrow (HOCH_2)_3P + (C_4H_9)_3\overset{+}{P}{-}CH_2OHCl^-\ .$$

The exchange of hydrocarbon groups between OPC can be catalysed by alkali metals[225]

$$(C_6H_5)_4\overset{+}{P}\overline{Br} + (p\text{-}CH_3C_6H_4)_2PK \rightarrow (C_6H_5)_3P + (p\text{-}CH_3C_6H_4)\,PC_6H_5\ .$$

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Analysis of published data has shown that organophosphorus compounds can enter into numerous reactions involving the intermolecular exchange of organic substituents at the phosphorus atom. The ability of OPC to participate in these reactions depends significantly on the coordination number of the phosphorus atom. Substituents bound to a tricoordinate phosphorus atom via N, O, and S atoms exchange most readily. The exchange of hydrocarbon groups at the C–P bond (including those at a tricoordinate phosphorus atom) proceeds with much more difficulty. Compounds of tetracoordinate phosphorus enter into exchange reactions under more severe conditions than the analogous derivatives of tricoordinate phosphorus.

There are no literature data concerning the exchange reactions of organic substituents attached to dicoordinate and pentacoordinate phosphorus atoms. Nor have there been any communications about the exchange of substituents bound to phosphorus via heteroatoms such as Se and Si. The exchange reactions of phosphorus isotopes, which are of interest from both practical and theoretical points of view, have been little studied.

It has been shown that the exchange reactions of organic substituents attached to the phosphorus atom can be greatly influenced by acid and basic catalysts; however, the role of the catalysis has been studied thoroughly only in reactions involving compounds of tricoordinate phosphorus[41,45,160,226,227].

Study of the mechanisms of reactions involving the intermolecular exchange of organic substituents attached to the phosphorus atom show that these reactions proceed via stages in which intermediates are produced[9,10,79]. The formation of an unstable intermediate has been established by ^{31}P NMR in reactions involving compounds of both tricoordinate[228] and tetracoordinate[229] phosphorus. Further development of this branch of the chemistry of OPC will be associated with a more profound study of the mechanisms and characteristic features of the exchange reactions.

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All-Union Institute of Phytopathology,
Golitsyno,
Moscow Region.

Translated from *Uspekhi Khimii*, 53, 825-852 (1984) U.D.C. 547.1'13

Organometallic Chelate Complexes of the $\pi-\pi$ and $\pi-n$ Type

N.I.Rybinskaya and V.V.Krivykh

Organometallic chelate complexes in which either organic fragments π-bonded to the metal (chelates of the $\pi-\pi$ type) or complexes where heteroatomic groups with an unshared electron pair (NR_2, PR_2, AsR_2, OR, etc.) linked to the metal via an n-type bond (chelates of the $\pi-n$ type) are present together with the π-bonded fragments are examined. Data on complexes with polydentate ligands, including different combinations of fragments π- and n-coordinated to the metal are also surveyed. The characteristic features of the formation of organometallic chelates of the $\pi-\pi$ and $\pi-n$ types, which depend on the properties of the chelating ligand and the nature of the metal, are discussed.
The bibliography includes 267 references.

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I. INTRODUCTION

Chelate complexes have found extensive applications in many fields of technology, medicine, and agriculture. The activity of complexones, pesticides, certain medicinal preparations, analytical reagents, etc. is based on their capacity for chelation. However, among such compounds, the so-called inorganic chelates, in which the bond between the metal and the ligand is achieved via a heteroatomic group, have been most widely and comprehensively investigated. Organometallic chelates in which at least one of the bonds of the chelating ligand and the metal atom or ion is a metal–carbon σ- or π-bond are much less well known and have been altogether very little investigated. These compounds are distinguished by a wide variety of types. At the same time the study of the problem of chelation in the chemistry of organometallic compounds of transition metals is important for a number of reasons. In the first place the increase of stability owing to the chelate effect makes it possible to synthesise and investigate new types of complexes. Furthermore, chelation is closely related to problems such as cyclisation, matrix synthesis, and the *cis*-effect. The chelate effect is also of practical importance; in particular, chelation is important in homogeneous catalytic reactions widely used in industry at the present time.

Studies on organometallic chelates began comparatively recently and have not so far been systematic. The main cause holding back the development of this field is lack of information about the characteristics of the formation of organometallic chelates. This review is an attempt at a survey of the data which have accumulated on the compounds indicated in order to discover both similarities between organometallic and inorganic chelates and differences due to the specific features of their coordinated organic ligands and the types of their bonds with the metal. The review analyses for the first time certain rules governing the formation as well as the characteristic features of the structures and geometries of organometallic chelates.

Since the significant differences between chelate compounds are determined by the nature of the coordinating group of the ligand and the bonds which they form with the metal, different chelate compounds can be classified in terms of the types of bond. Since three main types of bonds between the metal and the organic ligand are known [the n-bond (using the free electron pair of the heteroatom) and the σ- and π-bonds], in principle all chelates with bidentate ligands can form six types of complexes: $n-n$, $n-\sigma$, $n-\pi$, $\pi-\pi$, $\pi-\sigma$, and $\sigma-\sigma$ and the last five refer to organometallic chelates. In the present review attention has been concentrated on organometallic chelates with $\pi-\pi$ and $\pi-n$ bonds formed by bidentate chelating ligands containing two unsaturated fragments of the type C=C, C=X (X = N, O, or another heteroatom), C≡C, C≡N,  ,  ,  , and  (chelates of the $\pi-\pi$ type) or, together with the unsaturated fragment, they contain a heteroatomic group with an unshared electron pair of the type NR_2, PR_2, AsR_2, SR_2, OR, etc.) (chelates of the $\pi-n$ type); complexes with polydentate ligands forming π- and n-bonds in different combinations are also considered (chelates of these types constitute the most complex and interesting case). The synthesis and certain properties of chelate complexes with σ-coordination (intramolecular) have been recently described in a series of reviews[1-6] and in the present review we shall therefore consider only data for chelates of the $\pi-\pi$ and $\pi-n$ types.

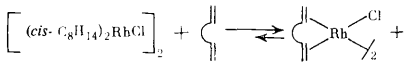
II. THERMODYNAMIC AND KINETIC CHELATE EFFECTS IN $\pi-\pi$ AND $\pi-n$ ORGANOMETALLIC CHELATES

There are no special grounds for the expectation of large differences between the thermodynamic and kinetic characteristics of the chelate effect (CE) in organometallic and inorganic chelates. However, a significant difference between the natures of the bond in organometallic compounds should lead to specific features which can be manifested in the properties of the bond between the metal atom and the coordinating group. Since the problem of stability is important in the chemistry of organometallic compounds of transition metals, the CE, as an effect involving an increase of stability, plays an important role. It is sufficient to state that the existence of many new types of compounds is due precisely to the CE. Furthermore, chelation and related phenomena, for example, synthesis in a matrix, are important for a homogeneous catalytic process. This is the reason for the importance of the analysis of the regularities and features characteristic of the CE in organometallic chelates.

Unfortunately, complexes with chelating ligands and the analogous complexes with related monodentate ligands are known in only a few instances. However, comparison of even

these scanty data shows that the complexes of monodentate ligands are as a rule less stable. For example, among the bismono-olefin complexes of metals, only rhodium(I) and iridium(I) complexes are stable, but their stability is again lower than that of the corresponding complexes with chelating diolefins. This is confirmed by the fact that, when a diolefin is added to complexes of this kind, a spontaneous reaction takes place with displacement of the mono-olefin and the formation of a diolefin complex. In complexes with volatile mono-olefins, the occurrence of such reactions can be explained (at least partially) by a shift of the equilibrium owing to the removal of the mono-olefin from the reaction sphere.

However, in the case of the complexes with cyclo-octene, one may claim, even in the absence of quantitative data, that the equilibrium in the reaction with cyclo-octa-1,5-diene[7] or cyclo-octatetraene[8] is almost wholly displaced to the right ($K \gg 1$) precisely as a result of the CE:



The question of the relative magnitudes of the CE in organometallic chelate complexes and of the dependence of this effect on various factors is much more complicated. Unfortunately there are very few quantitative data. Some of them are presented in Tables 1–4. The manifestation of the CE is supported by the formation constants of the silver complexes of unsaturated alcohols (of the π–n type) (Table 1).

Table 1. The formation constants (K, litre mol^{-1}) of Ag^+ complexes of unsaturated alcohols and their derivatives in water (partition method, 25 °C; reproducibility 10%)[9].

Olefin	K			
	X = H	X = OCOCH$_3$	X = OH	X = OCH$_3$
3-X-Prop-1-ene	—	0.35	12[a]; 22[b]	—
4-X-But-1-ene	—	0.31	26	—
5-X-Pent-1-ene	—	0.44	51	0.34
6-X-Hex-1-ene	0.095[a]	0.15	29	0.10
7-X-Hept-1-ene	—	<0.1	8.2	—
11-X-Undec-1-ene	—	<0.1	<0.1	—
5-X-5-Methylpent-1-ene	—	0.07	25	—
3-X-1-Methylenecyclohexane	0.096[c]	<0.1	19	—
3-(β-X-Ethyl)cyclopentene	0.119[c,d]	<0.1	38	—
5-X-Cyclo-octene	0.005[c]	<0.1	29	—

Note. $K = [\text{complex}]_{H_2O}/[\text{olefin}]_{CCl_4}[Ag]^+_{H_2O}$; [a] partition method[10]; [b] potentiometric method in water[11]; [c] value for cyclopentene[12]; [d] $K < 0.1$ for cyclo-octanol.

Thus the formation constant for *cis*-cyclo-oct-4-en-1-ol ($K = 29$) exceeds by several orders of magnitude the formation constants of the complexes with monodentate ligands of similar structure—*cis*-cyclo-octene ($K = 0.005$) and cyclo-octanol ($K < 0.1$). Analogous formation constants of the silver complexes of certain unsaturated alcohols have been obtained by the potentiometric method[13]. It is also noteworthy that, according to the data in Table 1 and Wilcox and Gaal[13], the character of the variation of the formation constants of chelate complexes as a function of the distances between the olefin and hydroxy-groups, considered in detail below, can be clearly traced. A similar trend in the variation of K has been observed[14] also for the reaction $Ag^+ + L \rightleftharpoons [AgL]^+$ (Table 2), where L are sulphur- and selenium-containing unsaturated ligands; however, the most interesting feature of this system is the fact that ΔH and not ΔS makes a decisive contribution to the CE.

Table 2. Thermodynamic parameters (kcal mol^{-1}) of the silver complexes[14]: $Ag^+ + L \rightarrow [AgL]^+$.

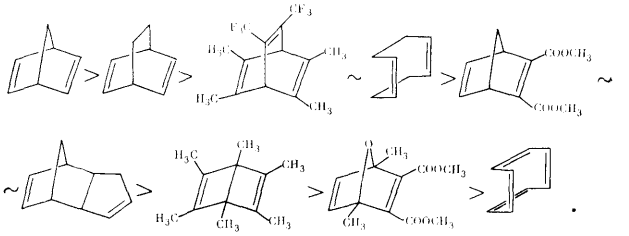
Ligand	$-\Delta G$	$-\Delta H$	$-T\Delta S$	$\delta(\Delta G)$	$\delta(\Delta H)$	$\Delta(T\Delta S)$
$C_4H_9SCH_2COO^-$	5.35	6.81	1.46	1.16	4.21	3.06
$CH_2{=}CH(CH_2)_2SCH_2COO^-$	6.51	11.02	4.52			
$CH_2{=}CH(CH_2)_3SCH_2COO^-$	5.71	8.39	2.68			
$C_4H_9SeCH_2COO^-$	6.24	7.79	1.55	0.78	5.23	4.42
$CH_2{=}CH(CH_2)_2SeCH_2COO^-$	7.05	13.03	5.97			
$CH_2{=}CH(CH_2)_3SeCH_2COO^-$	6.31	9.13	2.87			

The formation constants of silver complexes with various diolefins (complexes of the π–π type), listed in Table 3, illustrate the different contributions of the CE depending on the structure of the diolefin[15] (for comparison, Table 3 also includes complexes with mono-olefins of similar structure).

Table 3. The formation constants of the silver complexes of olefins in ethylene glycol at 40 °C[15] (gas–liquid chromatographic method).

Olefin	K, litre mol^{-1}	Olefin	K, litre mol^{-1}
But-1-ene	7.7	Cyclohexene	3.6
Buta-1,3-diene	4.2	Cyclohexa-1,4-diene	4.9
Penta-1,4-diene	10.2	1-Methyl-4-(2-propenyl)cyclo-hex-1-ene	5.9
Hexa-1,5-diene	28.8	4-Vinylcyclohex-1-ene	11.2
2-Methylhexa-1,5-diene	22.1	Norbornene	62
2,5-Dimethylhexa-1,5-diene	13.3	Norbornadiene	33.7
Hepta-1,6-diene	14.7	Cyclo-octa-1,3-diene	3.2
Octa-1,7-diene	11.3	Cyclo-octa-1,4-diene	14.4
Nona-1,8-diene	10.4	Cyclo-octa-1,5-diene	75
Deca-1,9-diene	7.8	Cyclo-octatetraene	91

The contribution of the CE is particularly large in the case of a cyclic diolefin—cyclo-octa-1,5-diene. For cyclic dienes, a marked dependence of the CE on the geometry of the chelating ligand has been observed and the equilibrium constants determined by the ^1H NMR method for the complexes [(diene)$RhCl_2$], vary by five orders of magnitude[16]. The chelating capacity of dienes diminishes in the following sequence:



Important results have been obtained by the direct determination of the enthalpies of formation (Table 4).[17]

The results show that in chelates of the π–*n* and π–π types both the entropy and enthalpy factors make an important contribution to the CE, as in inorganic chelates. The relative importance of these factors apparently varies as a function of the different features of the complexes.

The kinetic CE can be illustrated by data[18] obtained for the reaction

$$DQNi(diene) + P(OCH_3)_3 \rightleftarrows Ni[P(OCH_3)_3]_4 + DQ + diene,$$

where DQ is duroquinone and 'diene' is duroquinone, cyclo-octa-1,5-diene, *endo*-bicyclopentadiene, norbornadiene, and cyclo-octatetraene. It has been suggested that the first stage is the bimolecular reaction of trimethyl phosphite with the nickel complex in which one bond between the chelating diene and the metal is ruptured. The rate constants for this stage vary in the following sequence: DQ << cyclo-octadiene< bicyclopentadiene < norbornadiene < cyclo-octatetraene. The sequence obtained agrees with that found[19] on the basis of the ligand exchange reaction. Thus, in the given instance, the kinetic and thermodynamic CE act in the same direction.

Table 4. The heats of the reactions of chelating olefins and other ligands with $(CH_3CN)_2PdCl_2$ in methylene dichloride[17].

Ligand	$-\Delta H$, kcal mol^{-1}
Bicyclopentadiene	4.9±0.1
Cyclo-octatetraene	5.6±0.1
trans,trans,trans-Cyclododecatriene	5.9±0.1
1-Methyl-4-(2-propenyl)cyclohex-1-ene	6.8±0.3
Hexa-1,5-diene	8.0±0.4
Cyclo-octa-1,5-diene	13.0±0.4
Norbornadiene	13.3±0.8
Pyridine	26.0±0.7
Tetramethylethylenediamine	27.3±1.7
o-Phenylenebisdimethylarsine	35.2±0.7
Bis(diphenylphosphino)ethane	50.5±1.7

Together with quantitative thermodynamic and kinetic data, the decomposition temperatures as well as the results of physical methods of investigation and even qualitative chemical data are used to estimate the stabilities of the compounds. It is necessary to treat such results, particularly those of the last type, with caution. The overall stability of chelate π–π and π–*n* complexes is usually determined by the strength of the bond between the metal atom and the unsaturated fragment of the chelating ligand, since the heteroatom (possibly with the sole exception of oxygen) is usually more strongly bound to the metal (Table 4). However, this is true only when the complex does not contain other ligands bound still less strongly. The thermal stabilities of the compounds considered in terms of the thermodynamic and kinetic aspects should depend also on the mechanism of the decomposition reaction. In discussing the relative stabilities of the complexes on the basis of their decomposition temperatures (provided that these have been determined correctly), only data for isotypical complexes provide much information.

Physical methods as a rule give only indirect data about the metal–ligand bond strength. Infrared spectroscopy has been used most frequently for this purpose. For example, the shift of ν(C=C) on complex formation has been proposed[20–22] as a measure of metal–olefin bond strength. Since in the vast majority of cases the π–*n* and π–π chelates contain a double bond, one should note that this criterion can be used only to a first approximation. It has been found[23,24] that the vibration with the ν(C=C) frequency is not characteristic, since it is appreciably mixed with the δ(=C–H) deformation vibrations. It has therefore been suggested[25] that the overall percentage decrease of the ν(C=C) and δ(=C–H) frequencies in the coordination of an olefin be used. The frequency (or force constant) of the metal–olefin bond vibration can serve as another criterion[26]. However, few such data are available. Furthermore, the fact that the assignment of ν(C=C) on coordination (in many cases only tentative) has been carried out, with rare exceptions, only on the basis of infrared spectra without Raman spectroscopic data reduces the value of the results for the discussion of the stabilities of chelate complexes containing a double bond in the chelating ligand. Indeed it is difficult to discover a correlation between the character of the changes in the equilibrium constants[16] and the decrease of the vibrational frequency of the double bond on coordination in the complexes $[Rh(diene)Cl]_2$ (Table 5). On the basis of the values of ν(C=C), one can only assume that the strength of the M–$\overset{C}{\underset{C}{\|}}$ bond in the chelate complexes of this type is greater than that in the analogous complexes $[Rh(olefin)_2Cl]_2$ with monodentate olefins.

Table 5. The decomposition temperatures and changes in the stretching vibration frequencies of the double bond on coordination for complexes of the type $[Rh(diene)Cl]_2$ and $[Rh(mono\text{-}olefin)_2Cl]_2$.

Ligand	Decomp.temp.,°C	ν^{fl}(C=C)	ν^{c}(C=C)	$\Delta\nu$(C=C)
Norbornadiene	240 [27]	1550 [16]	1449 [16]	101 [16]
Norbornadiene	>170 [28]	—	—	150 [28]
Hexachloronorbornadiene	296—298* [29]	1604 [29]	1380 [29]	224
Bicyclo[2.2.2]octa-2,5-diene	—	1630 [16]	1430 [16]	200
Cyclo-octa-1,5-diene	>235 [30]	—	—	180 [28]
Tetrafluorobenzobarrelene	>270 [31]	—	—	—
Bicyclopentadiene	205 [32]	—	—	—
Hexamethylbicyclo[2.2.0]hexa-2,5-diene	—	1685 [16]	1505 [16]	180
Cyclo-octatetraene	145 [27]	1640 [16]	1412 [16]	228
Cyclo-octatetraene	—	1630 [8]	1410 [8]	220
Cyclodeca-1,6-diene	215—220 [32]	1650 [32]	1446 [32]	204
4-Vinylcyclohex-1-ene	>145 [33]	—	—	—
Hexa-1,5-diene	160 [34]	1642 [34]	1488, 1505 [34]	154, 137
2,5-Dimethylhexa-1,5-diene	>160 [28]	1646 [28]	1510 [28]	136
Cyclo-octene	>150 [28]	1650 [28]	1555 [28]	95
Cycloheptene	>115 [28]	1650 [28]	1560 [28]	90

Note. ν^{fl}(C=C) is the stretching vibration frequency of the double bond in the free ligand, ν^{c}(C=C) the stretching vibration frequency of the double bond in the coordinated ligand, and $\Delta\nu$(C=C) the shift of the stretching vibration frequency of the double bond on coordination.

* Melting point for fusion accompanied by decomposition.
Note. The numbers in square brackets denote references (Ed. of Translation).

Table 5 shows that the decomposition temperatures are in many instances better correlated with the strength of the bond between the metal and the ligand. Examination of the thermodynamic stabilities[16] (see above) and thermal stabilities (Table 5) of isotypical complexes leads to the same conclusion: complexes of norbornadiene and its analogues as well as those

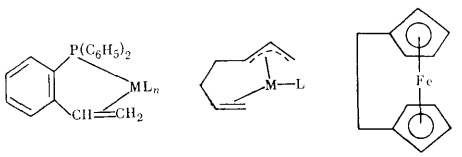
of cyclo-octa-1,5-diene are the most stable, while the complexes of *endo*-bicyclopentadiene and particularly cyclo-octatetraene are less stable.

In addition, the very fact of the formation of a chelate complex together with qualitative chemical reactivity data can be used to discuss various factors influencing the relative stabilities of the chelates.

III. THE INFLUENCE OF THE PROPERTIES OF THE CHELATING LIGAND ON THE STABILITY OF THE CHELATES

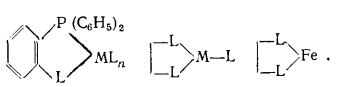
1. The Size of the Chelate Ring

The properties of chelate complexes are influenced most significantly by the nature of the chelating ligand, namely the nature of its coordinating groups, its geometry in the free state, the size and geometry of the bridging fragment separating the coordinating groups, and many other factors. However, before beginning the discussion of its influence, one must decide how to define the size of the chelate ring in π–*n* and π–π chelates. The point is that, in contrast to chelating ligands containing coordinating *n*- and σ-groups, ligands with π-fragments form chelate rings whose size is more difficult to define. We shall consider π–*n* and π–π chelates containing coordinating groups of different types:

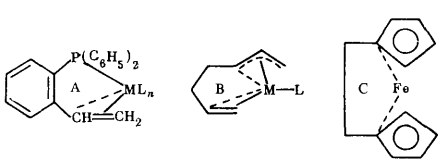


Even in the simplest case—in the chelate complex of diphenyl-*o*-styrylphosphine— the ring size can be defined in different ways. In the system of formulation for π-complexes usually employed a line connects the centre of the double bond with the metal atom. In this case one can assume that the size of the chelate ring amounts to 5.5 units[3,6]. When a metal–olefin bond is treated as a three-membered ring, we arrive at the conclusion that two rings are formed on chelation: a three-membered ring and a five-membered ring.

This treatment does not solve the problem in the case of more complex π-groups—allyl, butadiene, cyclopentadienyl, and arene, i.e. groups containing a system of conjugated bonds. However, one can propose a simple solution to this problem if one disregards the nature of the coordinating group and the latter is denoted by L, i.e. it is assumed that any coordinating group constitutes one unit in the ring. In this case the formulae of chelate complexes assumes the following form:

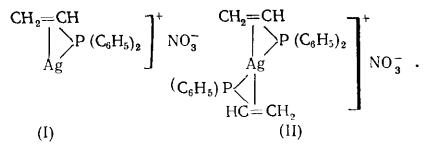


As a result, the chelate ring in the complexes considered must be regarded as five-membered. The activation of the chelate rings A, B, and C proper in these complexes leads to the same conclusion:



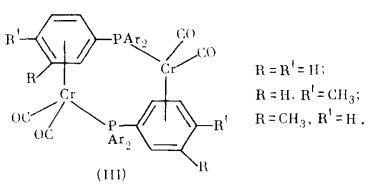
Despite the apparent arbitrary nature of this approximation, the latter "works" in most cases and, as will be seen from the foregoing, such calculations show that the greatest stability of the complexes and the maximum tendency towards their formation obtain in five- and six-membered rings, as for inorganic chelates.

For example, the simplest ligands which can form π–*n* chelates are heteroatomic substituted ethylenes. It is believed that diphenylvinylphosphine forms complexes (I) and (II) with silver cations[35]:



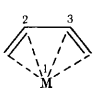
(I) (II)

Although the structure of the complexes has been assigned on the basis of a fairly broad set of data—analytical, spectroscopic (infrared, ^{1}H, and ^{31}P NMR), and cryoscopic—it cannot be regarded as finally established without resorting to X-ray diffraction analysis (XDA), particularly since chelation involving three-membered rings has not been observed in any one instance in the formation of metal complexes of heteroatomic substituted ethylenes. The fact that the formation of three-membered rings is unfavourable can sometimes lead to a dimeric product containing six-membered rings, as happens, for example, in the thermal interaction of $Cr(CO)_6$ with triarylphosphines. Here complexes (III) were isolated and acyclic compounds of the type arene. $Cr(CO)_2PAr_3$ were not detected[36].



(III)

Using the proposed method for the calculation of the number of units in the chelate ring, the numerous group of transition metal complexes with conjugated dienes should be classified as three-membered π–π chelates in terms of their formal features (see, for example, the relevant reviews[37–39]).



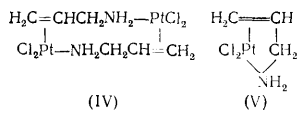
Indeed the term "chelates" is frequently used in the literature in relation to such compounds. However, we excluded them from consideration because the reduced energy of the antibonding π^* orbital of these ligands makes a significant contribution to the stability of complexes of this type (see, for example, Streitwieser[40] and Rybinskaya[41]), which masks the CE proper in these complexes.

Four-membered chelate rings are also relatively uncommon. Thus the high thermodynamic and kinetic stability of complexes of allyl alcohol, namely $[C_3H_5OH.PtCl_3]^-$,[42] can be explained by the additional coordination of the OH group to the platinum atom. This can also be indicated by the infrared spectra of compounds of the type of *trans*-$[C_3H_5OH.PtCl_2.amine]$ [a decrease of ν(OH) by 140–160 cm^{-1}].[43,44] An analogous situation has been noted for platinum complexes of β-hydroxyalkylacetylenes[43,44].

According to infrared spectroscopic data, in the 1:1 complex of C_3H_5OH with copper(I) chloride both the double bond [$\Delta\nu$(C=C) ≅ 95 cm^{-1}] and the OH group [$\Delta\nu$(C–O) ≅ 20 cm^{-1}] are coordinated. On this basis, a dimeric structure has been postulated for the chelating ligand CH_2=CH–CH_2OH.[45] The formation constant of the complex C_3H_5OH.CuCl is higher than that of the complex of C_3H_5Cl with CuCl.[46] A significant difference between the formation constants of the complexes with the $AgNO_3$ in water has been observed for C_3H_5OH and alkylethylenes (Table 1).[8,9]

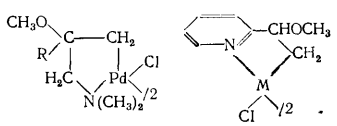
The higher heat of formation of complexes of the copper(I) halides CuCl and CuBr with allylamine compared with propylamine can also be explained by chelation[47] ($\Delta H_{C_3H_5NH_2} - \Delta H_{C_3H_7NH_2}$ = 10–12 kcal mol^{-1}). Infrared spectroscopic data [the decrease of the frequencies ν(C=C), $\nu(NH_2)$, and $\delta(NH_2)$] also agree with the chelate structure of the complexes.

The question of the formation of platinum(II) chelate complexes of $C_3H_5NH_2$ cannot be regarded as finally solved. On the basis of infrared spectra, it has been suggested[48] that, together with the dimeric form (IV)[49,50], the monomeric form (V) is present, albeit in a smaller amount:



(IV) (V)

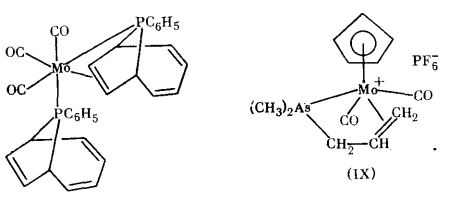
In addition, the intermediate formation of four-membered chelate rings of the π–n type[51,52] has been suggested in the interaction of $C_3H_5NH_2$ with palladium(II) salts[53] and also of 2-vinylpyridine with palladium(II) and platinum(II)[54] in methanol with subsequent conversion into stable five-membered n–σ chelate complexes (VI) and (VII)—the products of nucleophilic addition to the coordinated double bond:



(VI) (VII)

An analogous reaction of allyl- and propargyl-phosphines with platinum is also known[55].

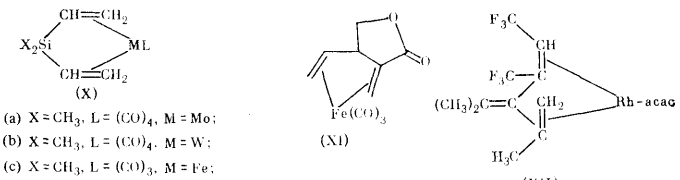
The structure of complexes (VIII) and (IX) with ligands containing a heteroatom in the allyl-position, namely 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene[56] and allyldimethylarsine[57], has been demonstrated more reliably:



(VIII) (IX)

The molecular weights were determined in these instances by osmometry or mass spectrometry. The relative stability of the four-membered chelate ring in compound (VIII) can be explained by the fact that the phosphorus atom is incorporated in a rigid bicyclic system. The formation of four-membered chelate rings is characteristic of bicyclic dienes (see below). The large radius of the arsenic atom in complexes (IX) can lead to the same result.

The formation of four-membered chelate rings with linear dienes is a fairly rare phenomenon. Such complexes of type (X) have been obtained from di- or tetra-vinylsilanes with molybdenum, tungsten[58,59], and iron[60,61] carbonyls [compounds (X, a–d)] and rhodium acetylacetonates[62] [compound (Xe)]:



(X)

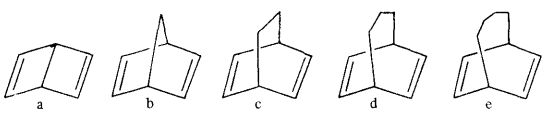
(a) X = CH_3, L = $(CO)_4$, M = Mo;
(b) X = CH_3, L = $(CO)_4$, M = W;
(c) X = CH_3, L = $(CO)_3$, M = Fe;
(d) X_2 = $(OC)_3Fe$  , L = $(CO)_3$, M = Fe;
(e) X = CH_3, L = acac, M = Rh.

(XI)

(XII)

Complexes (XI)[63] and (XII)[64] with linear 1,4-dienes, in which a carbon atom is a bridge separating olefinic groups, have been obtained recently. The structure of complexes (Xd), (XI), and (XII) has been demonstrated by X-ray diffraction.

Metal complexes with cyclic dienes in which the double bonds are also separated by carbon atoms are much more common. Cyclohexa-1,4-diene itself rarely behaves as a bidentate ligand (see, for example, Birch et al.[65])†, while its derivatives (XIII, a – e) with a bridge connecting the 1,4-positions have a geometry favouring chelation (see below).



a b c d e

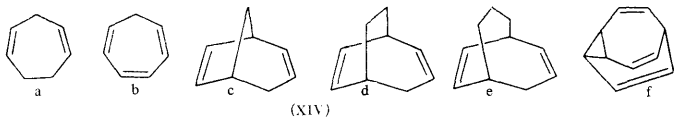
(XIII)

A single complex of palladium chloride with unsubstituted bicyclo[2.2.0]hexa-2,5-diene (Dewar benzene) (XIIIa) has been described[66], while complexes with the hexamethyl derivative of Dewar benzene are somewhat more common (see, for example, Huttner and Mills[67] and the references quoted therein).

Chelate complexes with bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) (XIIIb) are widely known. It is not possible to include these data in the present review and we shall therefore only refer to other surveys[37–39] and certain communications on X-ray diffraction studies[70–79]. Complexes based on bicyclo[2.2.2]octadiene (XIIIc)[16] or its derivatives[31,80,81] and bicyclo[2.2.3]nona-2,5-diene (XIIId) and its derivatives[82,83] have also been described. A complex of iron tricarbonyl with a ligand of type (XIIIe), in which the bridge consists of a conjugated diene coordinated to $Fe(CO)_3$, is known[84].

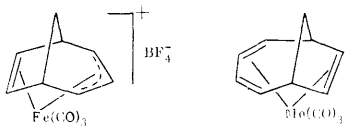
† The formation of stable complexes with quinones[68] and their isostructural analogues (1,4-difluoro-1,4-diboracyclohexa-2,5-dienes)[69] can be explained by a significant contribution of electronic factors (decrease of the energy of the π^* orbital of the ligand—see, for example, Rybin[68]). The geometrical factors are in this case apparently no less unfavourable than for cyclohexa-1,4-diene.

A four-membered ring is formed in chelates of cyclic 1,4-dienes and in the case of cyclohexa-1,4-dienes two four-membered rings are produced, while in other cases there is a possibility of the formation, together with a four-membered ring, of rings of another size, which happens in the case of cyclohepta-1,4-diene (XIVa)[85,86] and related compounds: cycloheptatriene (XIVb)[87], bicyclo[3.2.1]octadiene (XIVc)[88,89], and derivatives of bicyclo[3.2.2]nona-2,5-diene (XIVd)[83], bicyclo[2.3.3]deca-2,5-diene (XIVe)[90], and bullvalene (XIVf)[91].



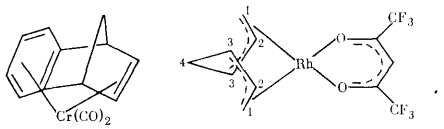
(XIV)

Several examples of chelate complexes of the π–π type with four-membered rings in which ligands other than olefins are present as one or both coordinating groups are also known. These are allylolefin[83,88,89,92–94] and diene-mono-olefin chelates[59,95]—for example in complexes (XV) (its structure has been demonstrated by X-ray diffraction[88]) and (XVI)[95]:



(XV) (XVI)

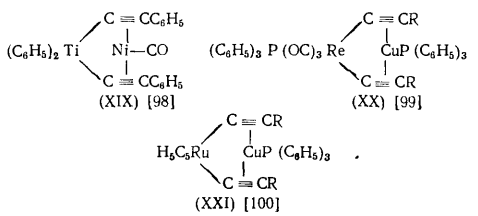
An arene ligand may function as one of the chelating groups, as happens in the chromium dicarbonyl complex of benzonorbornadiene (XVII)[96]. In compound (XVIII) both coordinating groups are π-allyl ligands[97]:



(XVII) (XVIII)

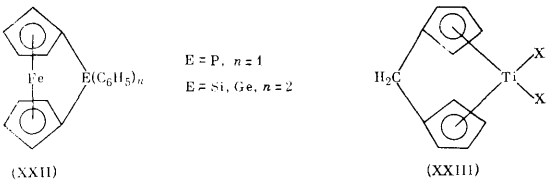
Here the chelating bis-π-allyl ligand is not incorporated in a bicyclic system, as in the cases described previously, and the chelate ring is therefore appreciably strained. The decrease of the Rh–C(1) and Rh–C(2) interatomic distances and partial rehybridisation of C(3) can be followed on the basis of X-ray diffraction data.

The increased stability of complexes (XIX)–(XXI)[98–100] with chelating diyne ligands# can be explained by the increased size of the atom separating the acetylenic groups, which should lead to a decrease of strain in chelate rings of this type. In addition, such strain depends also on the hybridisation of the atom indicated (see below):



Doubts have been expressed[102] about the results reported in a communication concerning dinitrile chelate complexes with the ligands $N{\equiv}C(CH_2)_nC{\equiv}N$ (n = 1–3)[101] involved in π-type coordination. See also Farona and Kraus[103].

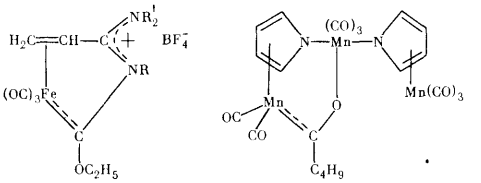
An analogous situation has been observed also in the case of ferrocenophanes, which can likewise be regarded as chelates. The replacement of a carbon atom by atoms with larger radii, namely silicon, germanium, and phosphorus, made it possible to obtain one-membered ferrocenophanes (XXII)[104], whose carbon analogues are unknown:



(XXII) (XXIII)

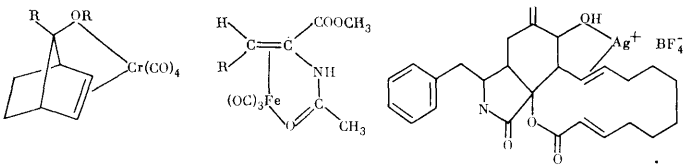
According to X-ray diffraction data, complexes (XXII) are appreciably strained[105]. On the other hand, the presence of a single carbon atom in the bridge is sufficient for wedge-shaped sandwich compounds—for example, compound (XXIII)[106].

Complexes containing five-membered rings are commonest among π–n and π–π chelates. In the case of π–n chelates a double bond and allyl, cyclopentadienyl, and arene groups function as the unsaturated fragment, while the atoms providing the electron pair for coordination are those of C, O, S, Se, N, P, and As. Examples of chelates in which a carbon atom is involved in n-type coordination are provided by the carbene complexes (XXIV)[107] and (XXV)[108] obtained recently:



(XXIV) (XXV)

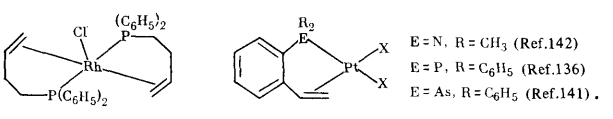
syn-Alkoxynorbornenes[109], acetamidoacrylates and acetamidocinnamates[110], and also the antibiotic Phomin[111], which form complexes (XXVI)–(XXVIII), have been used as oxygen-containing ligands:



(XXVI) (XXVII) (XXVIII)

The structure of compounds (XXIV), (XXV), (XXVII), and (XXVIII) has been established by X-ray diffraction.

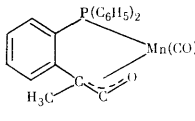
Ligands in which the 1-butenyl group is linked to oxygen[112], sulphur[113], selenium[114], and phosphorus[115–122] are fairly common. 2-Allylpyridine also has a geometry convenient for chelation[123,124], but ligands of the types considered which are most often employed are *o*-styryl derivatives of phosphorus[125–139], arsenic[137–141], or nitrogen[142]. Compounds (XXIX)[122] and (XXX), whose structure has been demonstrated by X-ray diffraction, have been quoted as examples:



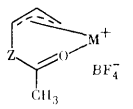
(XXIX) (XXX)

o-Styrylphosphine usually enters as such into the coordination sphere, but, on interaction with $CH_3Mn(CO)_5$, it is transformed into the oxoallylphosphine ligand [complex

(XXXI)][143]. Complexes with allyl [compound (XXXII)][144–146] or cyclobutadiene [compound (XXXIII)][147] and compound (XXXIV)[148]] fragments in the chelating ligand have also been obtained as a result of reactions in the coordination sphere of the metal and cyclobutadienes can be involved in the coordination of both η^2-type [compound (XXXIII)] and η^4-type [compound (XXXIV)].

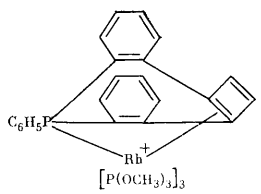


(XXXI)

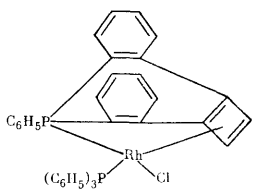


(XXXII)

Z = CH_2, M = $Fe(CO)_3$ (Ref.144)
Z = O, M = $Fe(CO)_3$ (Ref.145)
Z = CH_2, M = RhC_5H_5, IrC_5H_5 (Ref.146).

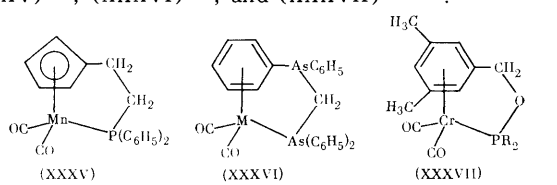


(XXXIII)



(XXXIV)

The following examples of cyclopentadienyl and arene chelate complexes of the π–n type are known: complexes (XXXV)[149], (XXXVI)[150], and (XXXVII)[151,152]:

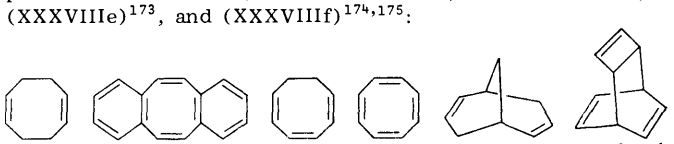


(XXXV) (XXXVI) (XXXVII)

(a) M = Cr; (b) M = Mo (a) R = C_6H_5; (b) R = OC_6H_5.

The structures of complexes (XXXI)[153], (XXXIII)[147], (XXXVIa)[154], and (XXXVIIb)[155] have been confirmed by X-ray diffraction.

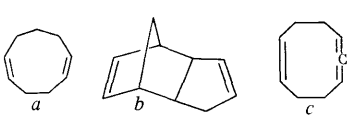
However, five-membered chelate complexes of the π–π type are undoubtedly the commonest. This applies primarily to complexes of cyclo-octa-1,5-diene (XXXVIIIa) (see, for example, Refs.37–39 and 156–169) and the related compounds (XXXVIIIb)[170], (XXXVIIIc)[171,172], (XXXVIIId)[37–39], (XXXVIIIe)[173], and (XXXVIIIf)[174,175]:



a b c d e f

(XXXVIII)

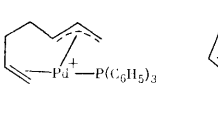
Complexes of cyclonona-1,5-diene (XXXIXa)[176] and compounds (XXXIX, b and c)[37–39,177–179] are close to this type of compound:



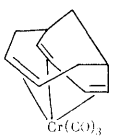
a b c

(XXXIX)

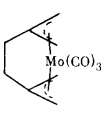
Complexes with linear dienes are fairly common among five-membered chelate complexes of the π–π type (see, for example, Refs.28, 34, and 180). The chain connecting the two double bonds can be incorporated in a six-membered ring[181,182]. One double bond can be endocyclic as, for example, in 4-vinylcyclohexene[183–185] or 5-methylenecyclopentene complexes[186]. Furthermore, various allylolefin [compound (XL)][187] (see also Lewis and Parkins[94]) or diene-olefin [compound (XLI)][188] (see also Ward and Pettit[189]), bisallyl [compound (XLII)][190], cyclopentadienylallyl [compound (XLIII)][191], cyclopentadienyldiene [compound (XLIV)][192], arene-olefin [compound (XLV)][193–195], arene-allene [compound (XLVI)][196], and arene-allyl [compound (XLVII)][197] chelates are known in addition:



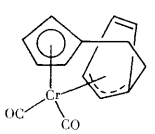
(XL)



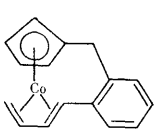
(XLI)



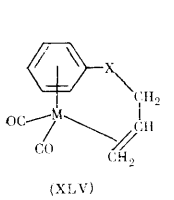
(XLII)



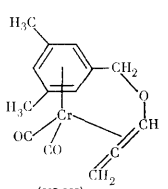
(XLIII)



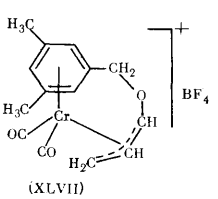
(XLIV)



(XLV)



(XLVI)

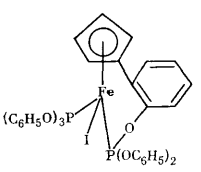


(XLVII)

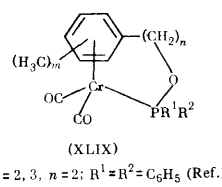
X = O, M = Cr; X = CH_2, M = Cr, Mo, W.

The structures of compounds (XLI) and (XLIV) have been established by X-ray diffraction. [2]Ferrocenophanes belong to chelates of the same type[5,198].

Although complexes with six-membered rings are encountered more rarely than those of five-membered rings, they are also fairly stable. As a rule, these are derivatives of platinum(II) and rhodium(I), which form the strongest bonds with olefins. The ligands of π–n type are mainly pentenyl derivatives of sulphur[113], selenium[114], phosphorus[116,120], and arsenic[199,200] as well as *o*-allylphenyl derivatives of phosphorus[128,129,201,202] or arsenic[201,202]. Complexes with *O*-alkyl-*N*-allyldithiocarbamates coordinated as bidentate ligands have been described[203–205]. Apart from olefin-containing six-membered π–n chelates, only the cyclopentadienyl chelate complexes (XLVIII)[206] and the arene chelate complexes (XLIX)[151,152,207–209] and (L)[210] are known. The structures of complexes (XLVIII)[211] and (L)[210] have been confirmed by X-ray diffraction:

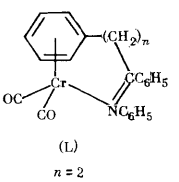


(XLVIII)



(XLIX)

m = 2, 3, n = 2; $R^1 = R^2 = C_6H_5$ (Ref.152)



(L)

n = 2

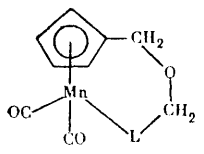
OC_6H_5 (Ref.151), F (Ref.205), ½  (Ref.206)

$R^1 = F$, $R^2 = OC_2H_5$ (Ref.207)

In some cases cyclodeca-1,6-diene does not exhibit chelating properties. Thus it forms a six-membered chelate with rhodium(I), gives rise to coordination polymers on reaction

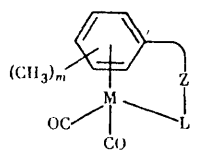
with palladium(II) salts, and does not react at all with platinum(II)[32,182,212]. The same can also be said of linear dienes, for example, diallyl ether[213-215]. The structure of some of its complexes has been established by X-ray diffraction[216,217].

Together with diene complexes, chelates containing one or two cyclic π-ligands of types (LI)[218], (LII)[193-196,219], and (LIII)[220] have been described:



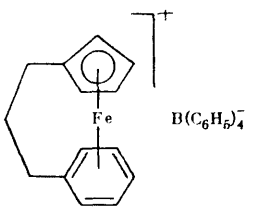
(LI)

L = CH=CH$_2$, C≡CH



(LIIa-e)

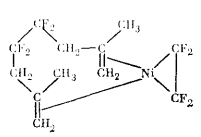
(a) M = Mo, W; Z—L = $(CH_2)_3CH{=}CH_2$;
(b) M = Cr; Z—L = $(CH_2)_3CH{=}CH_2$;
(c) M = Cr; Z—L = $CH_2OCH_2CH{=}CH_2$;
(d) M = Cr; Z—L = $CH_2OCH{=}C{=}CH_2$;
(e) M = Cr; Z—L = $CH_2OCH_2C{\equiv}CR$ (R = H, CH_3).



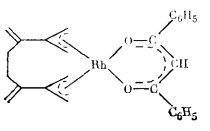
(LIII)

[3]Ferrocenophanes constitute the commonest type of six-membered π—π chelates[5,198].

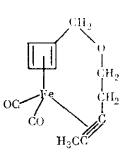
There are few data on compounds with seven-membered chelate rings. As examples, one may quote complexes (LIV)–(LVI)[221-223] (see also Refs.224 and 225). The structure of compound (LV) has been confirmed by X-ray diffraction. Apart from these, compounds (XLIX, n = 3, R = C_6H_5, or OC_6H_5)[151,152], (L, n = 3)[210], and (LII, Z–L = $CH_2CH_2OCH_2$–C≡CR)[219], as well as [4]ferrocenophanes[5,198] and [4]dibenzenechromophanes[226] contain a seven-membered chelate ring:



(LIV) (Ref.221)

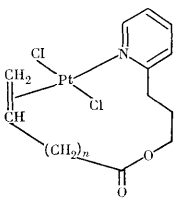


(LV) (Ref.222)



(LVI) (Ref.223)

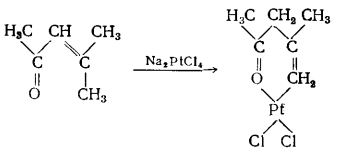
Chelates with medium and large rings are of special interest[152,198,227,228]. For example, complexes (XLIX, n = 4, R = C_6H_5 or OC_6H_5) contain eight-membered rings, while complexes (XLIX, n = 5, R = C_6H_5 or OC_6H_5) contain nine-membered chelate rings. The ease of formation of medium sized rings can be explained in this case[152] by the decrease of the extent of transannullar interactions compared with hydrocarbon rings of the same size. Fairly large numbers of ferrocenophanes containing rings of medium size and macrorings have been synthesised[198] and [5]bisarenechromophanes have also been obtained[226,229]. However, the increase of the stability of such complexes as a result of the CE is apparently either small or zero. This is confirmed by the finding that the olefinic end of the ligand in complex (LVII) can be displaced by ethylene[228]:



(LVII)

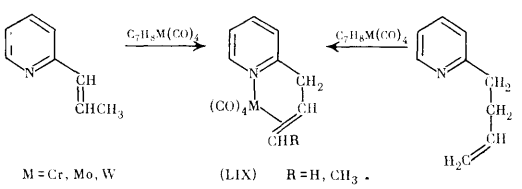
n = 1, 2, 4, 8.

Thus, despite the significant differences between the natures of the coordinating ligands, incorporating groups such as olefinic, allyl, cyclopentadienyl, etc., even a formal calculation of the number of units in the chelate ring reveals quite clearly a tendency towards the formation of the more stable five- and six-membered rings. Complexes (I) and (II) with three-membered rings are unique. Four-membered rings are also fairly rare with the exception of compounds with bicyclic dienes, which is due to the geometrical characteristic features of the latter. The lower stability of four-membered chelates compared with five-membered chelates is indicated by the fact that allyldiphenylphosphine forms chelate complexes neither with palladium(II) nor platinum(II), while butenyldiphenylphosphine forms them readily[117]. The use of divinyl ether was also unsuccessful, while hexa-1,5-diene gave a positive result[213]. The isomerisation of mesityl oxide under the influence of platinum(II) with formation of the mesityl iso-oxide complex (LVIII) containing a five-membered chelate ring is instructive. Even the loss of conjugation energy is compensated by the gain of chelate formation energy:



(LVIII).

The greater stability of five-membered chelate rings compared not only with four-membered but also with six-membered rings can be demonstrated by the reaction of 2-alkenylpyridines with norbornadiene complexes of Group VI metals[230]:

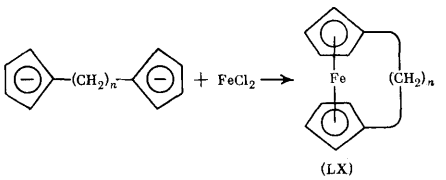


M = Cr, Mo, W (LIX) R = H, CH_3.

Isomerisation results only in the formation of complexes (LIX) containing five-membered chelate rings. The isomerisation of cyclo-octa-1,3-diene and cyclo-octa-1,4-diene under the influence of transition metals with formation of cyclo-octa-1,5-diene complexes is also consistent with these ideas[231-233]. The greater stability of five-membered rings compared with six-membered rings is also indicated by the interactions of 4-pentenyl and 3-butenyl derivatives of sulphur, selenium, and phosphorus with palladium(II). Only the 3-butenyl derivatives react with formation of five-membered chelates. It is of interest to note that platinum(II) forms chelates with both series of the above compounds[113,114,117]. The same can be said also of dienes, in which the double bonds are separated by two or three atoms[213]. The isomerisation of *o*-allylphenyldiphenylphosphine to the propenyl derivative[125,126] can also serve as evidence in support of the greater stability

of five-membered rings. This is also evident from a comparison of the relative reactivities of five- and six-membered chelates (see, for example, Garrow and Hartwell[117]).

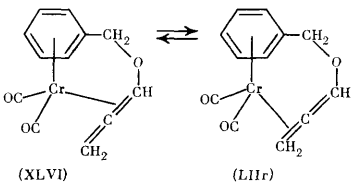
Yet another example illustrating the dependence of the CE on the size of the ring formed is provided by formation of ferrocenophanes in accordance with the following scheme:



(LX)

Thus the yield of a compound of type (LX) is 50% for $n = 2$, 2.5% for $n = 3$, 0.053% for $n = 4$, and 0.025% for $n = 5$.[198] The amount of polymeric products increases in the same sequence.

At the same time, chelates have been discovered in which the differences between the stabilities of the five- and six-membered rings are small. The chromium dicarbonyl complex with an arene-allene ligand gives rise in solution to an equilibrium mixture of the two forms corresponding to five-membered [compound XLVI)] and six-membered [compound (LIId)] chelates[196]. Unfortunately, this new instance of metallotropy has not been investigated adequately:



(XLVI) (LIIr)

The geometry of the ligand sometimes imposes a particular size on the chelate ring. Thus, in the case of arene-acetylene chelates of type (LIIe), six- and seven-membered rings are formed readily, while complexes with five-membered rings could not be obtained[219].

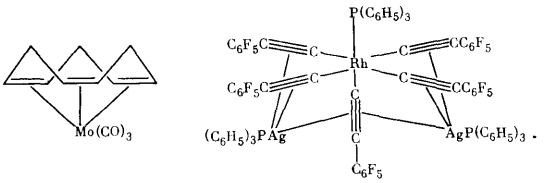
Quantitative data reflecting the dependence of thermodynamic stability on the size of the ring formed on chelation are available only for silver complexes[9,13-15,234], but they are satisfactorily correlated with qualitative data for other metals.

In conclusion of this Section one should note that approximately one-third of the known types of organometallic chelates have not been obtained as a result of specific synthesis but have been discovered accidentally as a result of the isomerisation of the ligand or its synthesis in the coordination sphere of the metal. In most cases this applies to five-membered chelates [compounds (XXIV), (XXV), (XXXI)–(XXXIV), (XL)–(XLIV), (XLVI), (XLVII), (LVIII), and (LIX)], but isolated examples of the synthesis of four-membered [compounds (XI), (XII), and (XVIII)], six-membered [compounds (XLVIII), and (LIId)], and seven-membered [compounds (LIV), and (LV)] complexes by this procedure are also known.

2. The Number of Rings

Studies on complexes with polydentate kn–$l\pi$- and $k\pi$-ligands were begun quite recently.

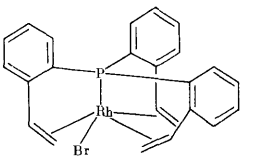
Complexes with polydentate $k\pi$-ligands ($k > 2$) have been little studied. Examples are provided by compounds (LXI)[235] and (LXII)[236] with ligands where three isolated double or triple bonds are coordinated to one metal atom. The structure of complex (LXII) has been established by X-ray diffraction:



(LXI) (LXII)

Ferrocenophanes with two, three, and four bridges[5,198] as well as bisarenechromophanes with two bridges[237,238] can be assigned to compounds of this type.

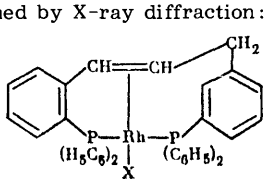
Complexes with kn–$l\pi$-ligands have been studied to a greater extent. Ligands potentially capable of forming five-membered rings have been synthesised for this purpose: tri(3-butenyl)phosphine[239], tri(4-pentenyl)phosphine[240], tri(*o*-vinylphenyl)phosphine[241,249], and tri(*o*-vinylphenyl)-arsine[242]. A rhodium(I) salt forms with these ligands penta-coordinate complexes of type (LXIII) whose structure, determined by X-ray diffraction[243,244], is trigonal-bipyramidal:



(LXIII)

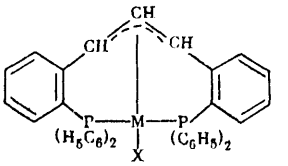
The double bonds are located approximately in the equatorial plane. Complexes with a similar structure have been obtained from phenyldi(*o*-vinylphenyl)phosphine[242] and dibutenyl-phenylphosphine[245]. On formation of complexes with Group VI metal[138,139], palladium(II)[246], and platinum(II)[246,247] carbonyls, these ligands react as bidentate species and in the case of palladium(II) and platinum(II) there is a rapid exchange of the coordinated and non-coordinated olefine groups according to ^{1}H NMR data. On the other hand, compounds containing two phosphorus atoms and one double bond [1,6-bis(diphenyl-phosphino)-*trans*-hexene and 1,6-bis(diphenylarsino)-*trans*-hexene] behave as tridentate ligands on formation of complexes with Group VI metal carbonyls[248].

Similar complexes with diphosphino-olefin ligands have been obtained also for other metals (see Bennett et al.[249] and the references therein and Clark[250]). The rhodium(I) complex (LXIV) has been quoted as an example[249]. Dehydrogenation of compounds (LXIV) leads to allyldiphosphinerhodium(I) complex of type (LXV). Other analogous derivatives (LXV) as well as complex (LXVI) with an allyl-dinitrogen ligand have also been obtained for other metals. The structures of compounds (LXV, M = Pd)[251] and (LXVI)[252] have been confirmed by X-ray diffraction:



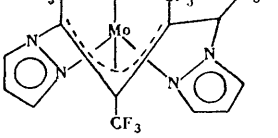
(LXIV)

X = Cl, Br



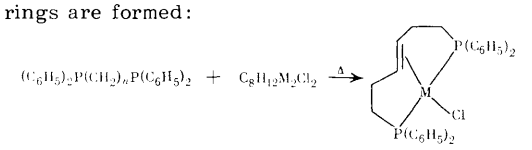
(LXV)

M = Pd; X = Cl; M = Rh, Ir, Ni; X = —



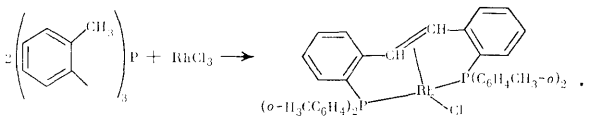
(LXVI)

It is noteworthy that, in the presence of a dehydrogenation catalyst, α,ω-bis(diphenylphosphino)alkanes form complexes (LXVII) with a tridentate diphosphino-olefin ligand only for $n = 6$,[250] i.e. only in the case where two five-membered chelate rings are formed:



M = Rh, Ir. (LXVII)

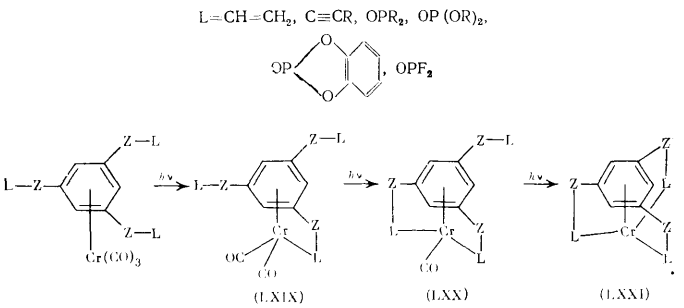
When $n = 5$, 7, or 8, complexes of type (LXVII) were not isolated. The tendency towards the formation of the analogous complex (LXVIII) with a conformationally more rigid chelating ligand [2,2′-bis(ditolylphosphino)stilbene] is so great that the ligand is generated in the coordination sphere of the metal from tri(*o*-tolyl)phosphine as a result of the dehydrogenation of the latter[253]:



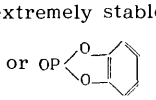
(LXVIII)

Similar reactions involving the formation of complexes with polydentate ligands as a result of dehydrogenation, isomerisation, and dimerisation have been investigated by Bennett and co-workers[135,253-258].

The characteristics of chelation with polydentate ligands have been studied systematically by Nesmeyanov and co-workers[259] in relation to arenechromium tricarbonyl complexes containing in the ω-position and in the side chain groups capable of coordination to metals:



(LXIX) (LXX) (LXXI)

Z are bridges consisting of $(CH_2)_n$ or various combinations of CH_2 and O. As a result, it has been found that the reaction is arrested at the single-bridge chelates (LXIX) when L = CH = CH_2 or $OPPh_2$ and at the two-bridge chelates (LXX) when L = $OP(OPh_2)$; all the CO ligands are substituted in succession with formation of extremely stable three-bridge ligands (LXXI) when L = OPF_2 or  .

Whereas the electronic factors in chelation are determined by the nature of the group L, the steric factors are determined mainly by the size of the bridge Z. Thus single-bridge chelates of type (LXIX) are formed starting with a two-membered bridge, while the two- and three-bridge chelates (LXX) and (LXXI) are formed only starting with a three-membered bridge. The three-membered bridge (six-membered chelate ring) proved to be optimal in the synthesis of polycyclic chelates of this type. The structure of the three-bridge complex (LXXI, Z–L = $CH_2CH_2OPF_2$) has been established by X-ray diffraction[260].

Thus the nature of the ligand plays a significant role in the formation of polycyclic chelates.

3. The Conformation and Geometry of the Ligand

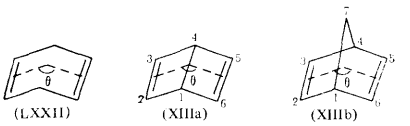
The question of the influence of the conformation of the ligand on the ease of formation of the chelates reduces to the elucidation of the number of possible conformations, their relative contributions, and, mainly, the conformation favourable for chelation. Apparently the greater the population of this favourable conformation, i.e. the conformation corresponding to the coordinated ligand, the greater the stability of the chelate complex. In the limiting case with a rigidly fixed conformation favourable for chelation, the contribution of this factor to the stability of the chelate complex should be a maximum. Indeed, a high stability has been observed in many cases for conformationally rigid ligands with a favourable disposition of the double bonds, such as, for example, norbornadiene and bicyclo[2.2.2]octa-2,5-diene[16] (Table 4).

Cyclo-octa-1,5-dienes[261] and cyclo-octatetraene[262], which have been shown to have the preferred boat conformation, form chelate complexes very readily; these have been obtained in large amounts with various metals. Cyclo-octadiene complexes are particularly stable (Tables 3 to 5).

The chair conformation of *cis*, *cis*-cyclodeca-1,6-diene is preferred to the boat conformation[263]. As a result, this ligand does not react with platinum(II) salts and its reaction with palladium(II) results in the formation of a polymeric complex[182]. On reaction with rhodium(I) derivatives at 80 °C, it gives rise to a chelate complex. This finding has been explained[32] by the fact that, at an elevated reaction temperature, the contribution of the boat conformation becomes considerable.

For linear ligands, the number of possible conformations is greater than for cyclic ligands and this number increases with increase in the length of the chain; the contribution of the favourable conformation therefore diminishes. Indeed, the stability of the complexes of linear ligands is lower (Tables 3 and 5). The decrease of the conformational mobility of the ligand results in an increase in the stability of the complexes formed. Thus *o*-allylphenyldimethylarsine and o-allylphenyldiphenylphosphine form chelate complexes with palladium(II) containing six-membered chelate rings[202], while pentenyldiphenylphosphine does not form such complexes[116]. This can be explained by the fact that, after the replacement of the C–C single bond in the chain by a multiple bond of the benzene ring, free rotation about this bond becomes impossible.

A significant change in geometry is observed in cyclic dienes, especially after the introduction of a bridge into the diene molecule. Only isolated examples of complexes have been described for cyclohexa-1,4-diene (LXXII) itself[65], but Dewar benzene[66,67] and norbornadiene[37-39,70-79] form complexes readily, which is probably due to the greater rigidity of the molecules owing to the presence of a bridge.



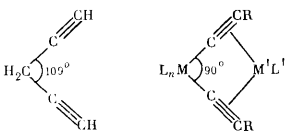
(LXXII) (XIIIa) (XIIIb)

The geometry of norbornadiene is particularly favourable for coordination to a metal, since in this compound the dihedral angle θ has the optimum value of approximately 115° and the

distance between C(1) and C(4) is increased to 2.24 Å, in contrast to Dewar benzene where it is approximately 1.55 Å; this reduces the extent of the non-bonding interactions of C(1) and C(4) with the metal atom on coordination[67]. It is interesting to note that an increase in the length of the bridge up to 2 and even 4 members causes little change in the geometry of the ligands[84,264] and the latter form stable complexes, like norbornadiene.

An important factor which diminishes the stability of chelate complexes with dienes is a non-parallel arrangement of the double bond. Such an arrangement is encountered in cyclic dienes with an odd number of atoms in the ring [the derivatives of cyclohepta-1,4-diene (XIV, a–f) and cyclonona-1,5-diene (XXXIX, a–c)], and also in dienes with an even number of atoms in the ring but with an asymmetric disposition of the double bonds (cyclo-octa-1,4-diene) or an asymmetric position of the bridge as in bicyclo[3.3.1]nona-2,6-diene (XXXVIIIe).

The geometry of the chelating ligand can depend on the nature of the atoms in the chain connecting two coordinating groups and also on their hybridisation. The replacement of a carbon atom in the chain of the diyne ligand (LXXIII) by the metal atom greatly reduces the angle between the acetylenic fragments which leads to a geometry of the ligand favourable for chelation. Complexes with ligands of type (LXXIV) are known[98–100], while no complexes have so far been obtained for the ligand (LXXIII). On the other hand, the formation of four-membered chelate rings by diolefin ligands requires an increase of the angle between the olefin fragments. This can be achieved by altering the hybridisation of the bridging carbon atom from sp^3 to sp^2, as shown in complex (XII)[64].



(LXXIII) (LXXIV)

4. The Nature of the Coordinating Groups

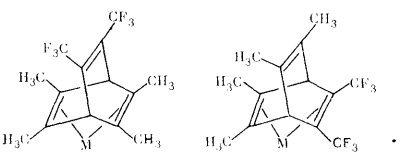
This problem has so far been little studied. In terms of the bond strength, the coordinating fragments can be arranged in the following sequence (for metals in a low oxidation state): P > As > N > unsaturated ligand > O; Se > S ≫ O (see also Table 4). Chelate complexes with a heteroatom can be arranged in the same sequence in terms of their stability. The data in Table 2 show that the stability of the selenium-containing chelate complexes of silver is higher than that of the corresponding sulphur-containing complexes. Chemical data are also consistent with this finding. Thus, in the case of alkenyl sulphide complexes of palladium(II) and platinum(II), *p*-toluidine fully substitutes the ligand, while in the alkenyl selenide derivatives only the double bond is displaced[113,114]. On the other hand, the substitution of the double bond C=C in the pentenylarsine complexes of platinum(II) by *p*-toluidine requires prolonged refluxing[200]. These complexes are as a rule more stable than the diene complexes. For example, diphenyl-*o*-styrylphosphine substitutes norbornadiene in Group VIB metal complexes with formation of complexes of type (XXX)[127].

The influence of substituents in the coordinating groups has not been studied systematically. It is evident from the available data that the introduction of even one alkyl substituent into a coordinating unsaturated group as a rule destabilises the chelate (Tables 1 and 3) and this is manifested even in the case of cationic silver complexes, the opposite behaviour being observed in the corresponding non-chelate mono-olefin complexes. Steric effects probably play a major role in organometallic chelates.

IV. THE INFLUENCE OF THE NATURE OF THE METAL ON THE STABILITY OF THE CHELATES

The stability of the chelate π–*n* and π–π complexes as a function of the nature of the metal varies as a rule in parallel with the stability of complexes of a similar structure containing non-chelating ligands. Thus the stability of the mono-olefin complexes of platinum(II) is greater than that of the analogous palladium(II) compounds. The same relative stabilities are observed also for chelate complexes with ligands containing a double bond. The CE does not as a rule alter the tendency in the variation of the stability but merely enhances it. The study of the dependence of the properties of the complexes on the metal is complicated by the fact that a sufficiently correct comparison is possible only for complexes containing the atoms of metals belonging to a single subgroup. Such a comparative study has been carried out by infrared and Raman spectroscopic methods for diene complexes of metals with the d^8 electron configuration and identical geometries of the compounds[30,34]. This led to the conclusion that the stability of the hexa-1,5-diene and cyclo-octadiene complexes of palladium(II), platinum(II), and rhodium(I) increases in the sequence indicated from palladium(II) to rhodium(I).

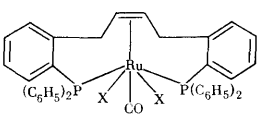
Depending on the nature of the metal, 2,3,5,6-tetramethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene can be coordinated in two ways: (LXXV) and (LXXVI):



(LXXV) (LXXVI)

A complex of type (LXXVI) is formed for M = $Mo(CO)_4$ or C_5H_5CO[80] and a complex of type (LXXV) for M = $[RhCl]_2$ or $Rh(Ph_3P)Cl$[16]; when M = $Fe(CO)_3$, complexes of both types are formed with the complex of type (LXXV) predominating[80].

It is noteworthy that in the case of chelates it is possible to obtain complexes with a metal–olefin bond in which the metal is in a higher oxidation state than is possible for non-chelate mono-olefin ligands. An example is provided by ruthenium(II) complexes of type (LXXVII)[156]:



(LXXVII)

X = Cl, Br.

The formation of such complexes is important primarily because the analogous compounds with monodentate and olefinic ligands occur as intermediates in catalytic processes and cannot be isolated because they are extremely unstable. Indeed, ruthenium(II) complexes of mono-olefins have not been isolated.

In contrast to inorganic chelates, the influence of metal atomic radius on chelate stability is low, since its variation for transition metals in Periods I–III in the zero oxidation state is insignificant (within the limits of 0.1 Å)[265]. The degree of oxidation exerts a major influence on the radius variation.

Specific valence angles α, which determine the geometry of the complex, are characteristic of each metal atom, depending on its nature, degree of oxidation, and ligand environment. It is interesting to examine this problem in relation to diene ligands used most frequently and forming the most stable complexes—norbornadiene and cyclo-octa-1,5-diene. Complexes of metals with square [for example, palladium(II), platinum(II), and rhodium(I)] and octahedral [for example, Group VI metals, ruthenium(II), etc.] configurations ($\alpha = 90°$) form somewhat more stable compounds with norbornadiene[37–39] (see also Table 4). The stability of tetrahedral norbornadiene complexes {for example, the complex Ni(O)-[(duroquinone)Ni(diene)]}, is lower than that of complexes containing less rigid ligands—cyclo-octadiene and bicyclopentadiene[18,19]. Group IB metals (valence angles $\alpha = 109°$, 120°, and 180°), characterised by a tendency towards linear hybridisation which increases from copper(I) to gold(I)[266], do not form cationic chelate complexes with norbornadiene§. Complexes in which norbornadiene behaves as a monodentate ligand were isolated later[267].

Not one chelate complex of the π–*n* or π–π type is known for gold(I). Only the powerful chelating ligand *o*-phenylenebisdimethylarsine forms a chelate complex with a tetrahedral configuration: $[(\text{diarsine})_2\text{Au}]^+\text{I}^-$.[266]

According to X-ray diffraction data, in complexes with a trigonal-bipyramidal configuration (valence angles 90° and 120°), ligands such as norbornadiene and cyclo-octadiene occupy one axial and one equatorial position ($\alpha = 90°$) and not two equatorial positions ($\alpha = 120°$), which also reflects the importance of the correspondence between the valence angles of the metal atoms and the geometry of the ligands.

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Summarising this review, one may say that organometallic chelate complexes constitute a new rapidly developing field in the chemistry of organometallic compounds. A large number of various chelate complexes of this type, among which polycyclic chelates are of special interest, have now been obtained. At the same time, the properties of organometallic chelates have so far been inadequately studied and the information available on this topic is in the main qualitative. Nevertheless, one may conclude that, in terms of many of their properties, organometallic chelates resemble inorganic chelates. This similarity is manifested primarily by the fact that in complexes of both types the five- and six-membered rings are the most stable, that the stability of the complexes increases with increase of the number of chelate rings in the molecule and with increase of the rigidity of the ligand, and also that both the entropy and enthalpy factors make an important contribution to the CE. At the same time, organometallic chelates have a whole series of characteristics associated primarily with the geometry of the organic ligand and the nature of the metal–carbon bond. Whereas the M = L bond in inorganic chelates is of the donor–acceptor type (*n*-type) and an increase of electron density at the heteroatom in the group L stabilises this bond, in organometallic chelates (where L is an organic π-ligand) the type of the metal–ligand bond is different. It is a combination of donor–acceptor and dative bonds. The nature of this π-bond makes its impression also on the geometry of the molecules of organometallic chelates. The metal atom in such complexes is as a rule located in a plane perpendicular to that of the π-ligand and not on the axis of the bond between the metal and the coordinating atom, as happens in inorganic chelates. Whereas the latter involve mainly metal cations, among organometallic chelates complexes of metals in a low oxidation state occupy a major place, which not only greatly extends the region of existence of chelate complexes in general but also makes it possible to expect that they will manifest new useful properties. For example, organometallic chelates with an increased electron density at the metal atom may prove to be active reductants or electron transferring agents, preserving at the same time the structure of the complex. The increase of stability as a result of the CE makes it possible to synthesise and investigate new types of organometallic complexes, information about the structure of which can throw light on the mechanisms of many catalytic processes. Finally, these complexes can themselves prove to be active catalysts, which has been confirmed by the isolation of some of them in catalytic reactions.

§ The only exception is that of the relatively unstable copper(I) complex of 7-t-butylnorbornadiene to which a chelate structure has been attributed solely on the basis of the ^{1}H NMR spectrum[267].

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Nesmeyanov Institute of
Organoelemental Compounds,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 853-879 (1984) U.D.C. 547.362

Propargyl Compounds in the Synthesis of Carbocycles and Heterocycles

S.F.Karaev, Sh.V.Garaeva, and A.M.Sladkov (deceased)

Data on the conversion of propargyl compounds into carbocycles and heterocycles are surveyed. The bibliography includes 181 references.

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I. INTRODUCTION

The cyclisation reactions of propargyl compounds have been the object of a comprehensive study in view of their importance for theoretical and synthetic organic chemistry. The characteristic features of the cyclisation of propargyl compounds are in many respects determined by their tendency to undergo rearrangements, Michael addition reactions, and diene and carbene syntheses.

The increased interest in the cyclisation of propargyl compounds is caused, apart from the need to solve theoretical problems, by their enormous role in the synthesis of carbocycles and heterocycles otherwise difficult to obtain, which can serve as the starting materials for the preparation of natural products and medicinal drugs.

Derivatives of isoquinolines[1], pyrimidines[2], pyranoflavans[3], and pyranoacridones[4], which occur in natural condensed systems, many vitamins, and antibiotics, have been obtained from propargyl compounds. For example, we may note the synthesis of a natural antibiotic—the lactone of 4-hydroxy-2-vinyl-but-2-enoic acid—from propargyl vinyl ether[5], of hydroxypyrones with a broad spectrum of biological activity from propargylvinyl alcohols[6], of aryldihydroisoquinolines, which are intermediates in the synthesis of alkaloids, from propargylbenzylamines[1], and of oxazoles, which are intermediates in the synthesis of vitamins B_6, from *O*-propargyliminoesters[7]. The antihypertonic activity of *N*-(guanidinoalkyl)pyrrolidines, synthesised from tertiary homopropargyl alcohols[8], has been noted and synthetic lignan lactones have been obtained by the intramolecular diene synthesis from propargyl propiolates[9].

In view of the undoubted practical value of acetylenic compounds of this type, there has been a considerable growth in interest in their cyclisation reactions in recent years. A monograph[10] and a number of reviews[11-16] have been published on the chemistry of acetylenic compounds, but they do not deal with the problem under consideration in terms of the cyclisation of propargyl compounds. In the present review an attempt is made to arrange systematically the studies in the last ten years on the cyclisation of propargyl compounds. Data published before 1971 are considered in those cases where this is necessary for the purposes of exposition.

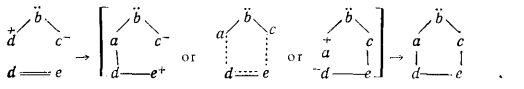
II. CYCLOADDITION

The cyclisation reactions of unsaturated systems in which rings are formed solely as a result of the rupture of π-bonds without the elimination of any fragment are known as cycloaddition reactions. These reactions constitute a universal method for the synthesis of various carbocyclic and heterocyclic systems. They include, for example, the widely familiar carbene and diene syntheses, 1,3-dipolar cycloaddition, and [2 + 2]cycloaddition.

Cycloaddition reactions with participation of ethynyl compounds have been most fully examined in a monograph[10].

1. 1,3-Dipolar Cycloaddition

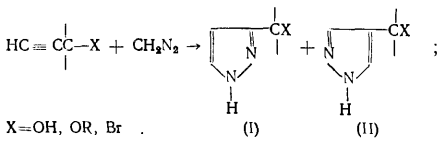
A clear-cut classification of 1,3-dipolar cycloadditions has been devised by Huisgen[17]. According to Huisgen's definition, any compound *a*–*b*–*c*, in which the atom *a* has an electron sextet and is a positive centre, the atom *c* has a free electron pair and carries a negative charge, and the atom *b* usually possesses an unshared electron pair, can constitute a 1,3-dipolar system. Problems of the mechanism of the 1,3-cycloaddition have been frequently discussed in the literature[18-20] and can be represented in a general form as follows:



Diazoalkanes, azides, nitrile ylides, nitrile imines, and nitrile oxides are typical 1,3-dipoles.

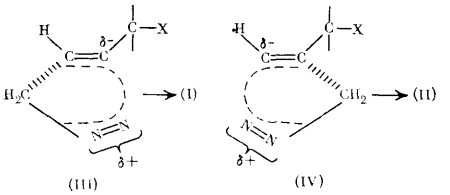
(a) Cycloaddition of Diazoalkanes

When propargyl compounds interact with diazoalkanes, substituted pyrazoles are formed. Thus the cycloaddition of diazomethane to propargyl alcohols, propargyl ethers, or propargyl bromides leads to two pyrazole isomers[21-23]:



X=OH, OR, Br . (I) (II)

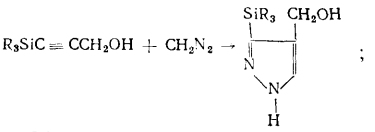
The ratio of the isomers depends on the nature of the substituents. Thus in the case of methylphenylethynylmethanol mainly the isomer (II) is formed; on the other hand, the main product of the reaction of propargyl bromide is the isomer (I). The reaction apparently proceeds via the transition states (III) and (IV):



(III) (IV)

It has been established[24] that the mode of 1,3-cycloaddition of substituted propargyl compounds to diazomethane is independent of the steric effect of the substituents and the electrostatic effects and that the decisive factor is the nucleophilic and electrophilic properties of the atoms between which a bond is formed.

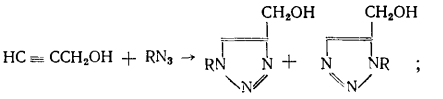
Pyrazoles are also produced in the interaction of propargyl compounds with substituted diazoalkanes. Propargyl alcohols and propargyl ethers react with methyl- or dialkyl-diazomethanes[21,25] to form exclusively an isomer of type (I), while an isomer of type (II) is obtained only from phenyl-substituted propargyl alcohols and ethers. Similar pyrazoles are also formed in the interaction of trifluorodiazoethane with propargyl bromide[26]. C_{sp}-trimethyl- or triphenylsilyl-substituted propargyl alcohols[27,28] are capable of entering into this reaction, an isomer of type (II) being mainly formed:



R=CH$_3$, C$_6$H$_5$.

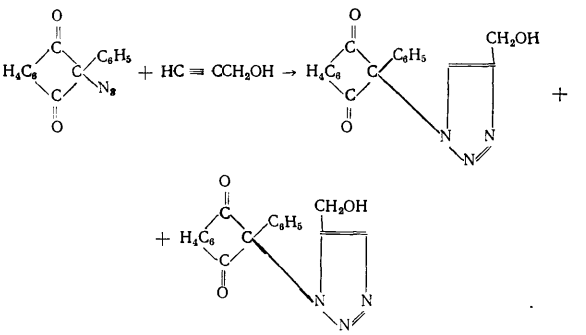
(b) Cycloaddition of Azides

The cycloaddition of azides to propargyl compounds leads to the corresponding triazoles, for example[29]:

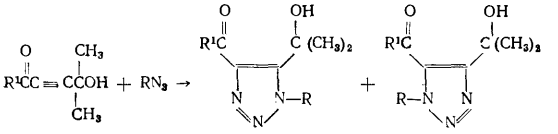


R=C$_6$H$_5$, C$_6$H$_5$CH$_2$.

2-(4-Hydroxymethyl-1,2,3-triazol-1-yl)- and 2-(5-hydroxymethyl-1,2,3-triazol-1-yl)-2-phenylindan-1,3-diones are formed from 2-azido-2-phenylindan-1,3-dione and propargyl alcohol[30]:



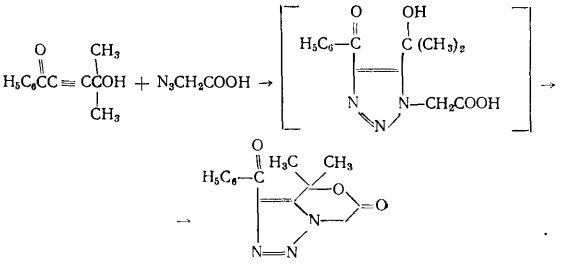
The ease of the cycloaddition of azides to propargyl compounds depends on the nature of the substituent at the triple bond and the structure of the azide. C_{sp}-bromo-substituted propargyl alcohols are less reactive than the unsubstituted alcohols[31]. Tertiary propargyl alcohols react with benzyl azide to form triazoles more readily than in the reaction with phenyl azide. The reactions of organic azides with the Iotsich reagent, obtained from propargyl alcohol, do not lead to cyclic compounds[32]. C_{sp}-acyl-substituted propargyl alcohols can also enter into the 1,3-cycloaddition reaction[33]:



Here the main factor determining the direction of the reaction is the high polarisation of the conjugated ketoethynyl system, which is responsible for the preferential formation of 1-R-4-acyl-substituted 1,2,3-triazoles. However, when aryl azides are introduced into the reaction, such regioselectivity is not observed. The ratio of the 4- and 5-acyl-substituted isomers changes in this instance towards an increase in the content of the latter.

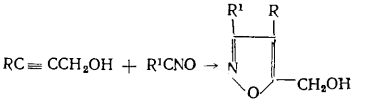
It is noteworthy that electron-donating (alkyl) substituents in the azide facilitate cycloaddition while electron-accepting substituents hinder it.

In certain cases the cycloaddition of azides to C_{sp}-acyl-substituted propargyl alcohol is accompanied by secondary processes involving the functional groups of the azide and the propargyl component. Thus azidoacetic acid reacts with benzoylethynyldimethylmethanol to form 4-benzoyl-1-methoxycarbonyl-5-(1-hydroxy-1-methylethyl)-1,2,3-triazole, which readily undergoes lactonisation:

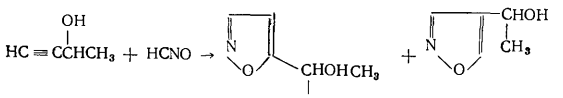


(c) Cycloaddition of Nitrile *N*-oxides

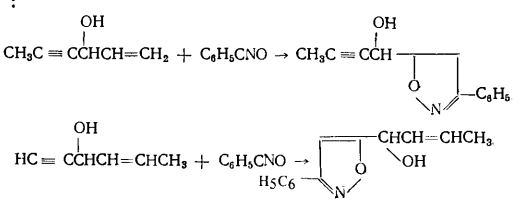
Propargyl alcohols readily react with nitrile oxides to form isoxazole derivatives[34,35]:



Secondary propargyl alcohols give rise to a mixture of isomeric isoxazoles[36]:



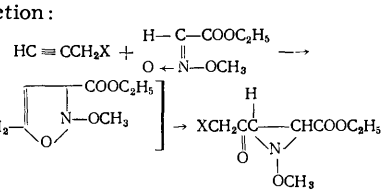
When benzonitrile oxide interacts with secondary vinylpropargyl alcohols, the addition can involve the double or triple bond depending on the structure of the initial compound[37]:



The 1,3-cycloaddition of nitrile oxides to propargylamines also leads to isoxazole derivatives[38].

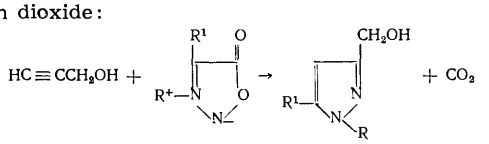
The mechanism of the formation of isoxazoles has been determined from the amount of incorporated deuterium[39]. It has been suggested that isomeric isoxazoles are obtained either directly via 1,3-dipolar cycloaddition or via the intermediate formation of the oxime $RC(=NOH)C\equiv CR^1$ with subsequent cyclisation. In the presence of D_2O isoxazoles free of deuterium are formed in the former case and [4-D]-isoxazoles are the products in the latter case.

Aziridine derivatives are formed in the reaction of propargyl alcohol and propargyl chloride with nitronic ester[40]. This is apparently associated with the rearrangement of the substituted 4-isoxazoline obtained in the first stage of the reaction:

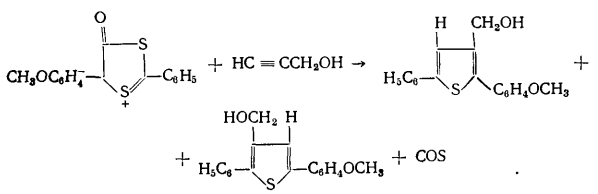


(d) Other Cycloaddition Reactions

Mesoionic compounds can also be regarded as 1,3-dipoles. They can form five-membered rings on reaction with propargyl compounds. Thus the interaction of 3-R-4-R^1-sydnone with propargyl alcohol leads to the formation of a pyrazole derivative[41]. Here the sydnone reacts via a [3 + 2]cycloaddition mechanism with simultaneous elimination of carbon dioxide:



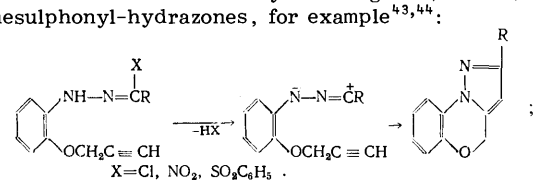
In the cycloaddition of mesoionic 1,3-dithiolones to propargyl alcohol, carbonyl sulphide is split off and a mixture of isomeric thiophens is formed[42]:



(e) Intramolecular Cycloadditions

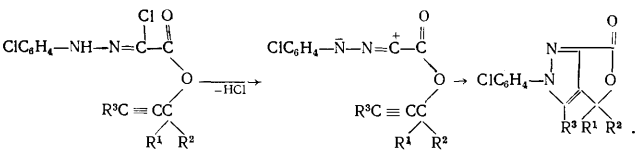
The reaction involving cycloaddition to propargyl compounds can occur not only intermolecularly but also intramolecularly. Such reactions involve molecules containing the necessary functional groups[17] (in a particular instance a 1,3-dipolar and a propargyl fragment).

The intramolecular cycloaddition of propargyl-substituted nitrile imines leads to the corresponding condensed pyrazoles. The sources of nitrile imines may be halogeno-, nitro-, and benzenesulphonyl-hydrazones, for example[43,44]:



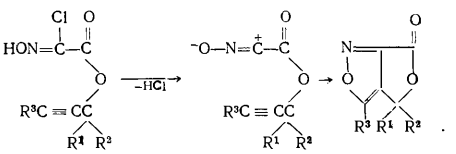
The ease of ring closure depends on the nature of the substituent R in the nitrile imine residue. In the case of the CH_2OH group, cyclisation does not occur.

The elimination of hydrogen chloride from "propargyl oxalate chlorohydrazone" leads to the formation of nitrile imines in which there is a possibility of intramolecular cycloaddition[45]. This results in the formation of furopyrazole derivatives:

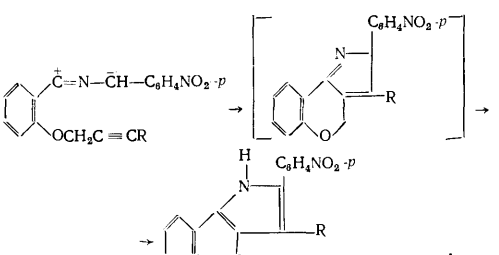


An analogous behaviour has been observed for "propargyl oxamide chlorohydrazone" but here the product is a mixture of isomeric pyrazoles[46].

Nitrile oxides with a propargyl fragment also readily undergo intramolecular cycloaddition. When "propargyl oxalate chloro-oximes" are heated in benzene in the presence of triethylamine, isoxazole derivatives are formed[45]:

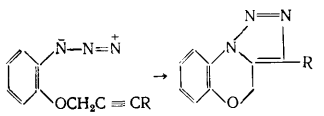


Benzopyranoisoxazole has been synthesised analogously[47]. It is noteworthy that the first reaction is structurally selective—only traces of the second isomeric adduct are formed, while both isomers are produced in the last reaction. Propargyl-substituted nitrile ylides are converted into benzopyranopyrrole derivatives as a result of intramolecular cycloaddition[48]:

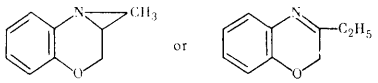


C_{sp}-Phenyl-substituted propargyloxy-derivatives give rise to pyrrole in a low yield (6%) under these conditions, which can be accounted for by the steric hindrance due to the C_6H_5 group.

Aryl azides containing the propargyloxy-group are converted into triazolobenzoxazines on intramolecular cycloaddition[49]:

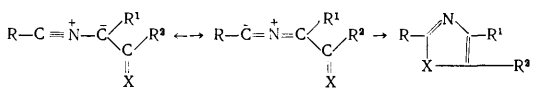


This is the first example of the intramolecular cycloaddition of the azide group to a triple bond. It is noteworthy that, in contrast to propargyl-substituted azides, azides with allyl groups form unstable Δ^2-1,2,3-triazolines, whose subsequent decomposition with elimination of molecular nitrogen gives rise to the reaction product:



2-Propargylthiophenyl azide undergoes analogous heterocyclisation to triazolobenzothiazine.

The intramolecular cycloaddition of nitrogen-containing analogues of propargyl-allenyl dipoles via the mechanism

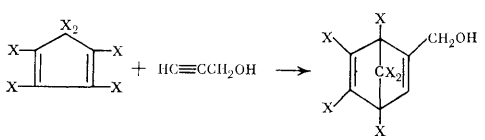


is of considerable interest. These reactions have already been surveyed and examined in a review[51].

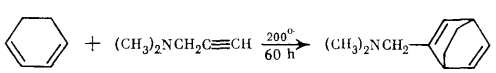
2. The Diene Synthesis

The Diels–Alder reaction belongs to the class of thermally allowed concerted processes[52], which means that unexcited molecules having 4π and 2π electrons respectively are combined. The diene synthesis has been discussed in detail in monographs[10,53,54] and in a review[19].

Propargyl compounds are active dienophiles. Thus propargyl alcohol reacts with hexachlorocyclopentadiene[55–57] and cyclopentadiene[58] at 130–150 °C to form the corresponding bicycloheptadienes:

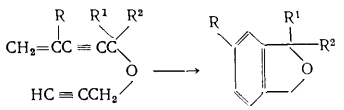


Propargyl chloroacetates[59,60] as well as the propargyl esters of trihalogenoacetic acids[61] react with the above dienes under analogous conditions. The yield of the adducts of the propargyl esters of trihalogenoacetic acids with hexachlorocyclopentadiene increases with increase of the atomic number of the halogen, while the opposite behaviour is observed for the adducts with cyclopentadiene. The reaction of dimethylpropargylamine with cyclohexadiene leads to cyclisation products in accordance with the mechanism[62]:

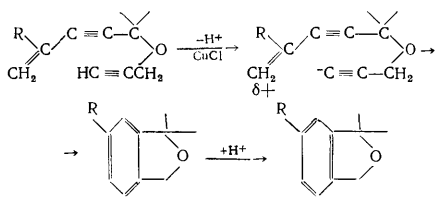


The reaction with the amine hydrochloride proceeds analogously. Allyldimethylamine does not react with cyclohexadiene under these conditions.

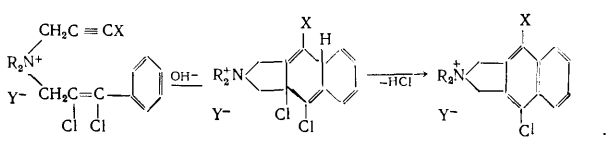
Propargyl compounds in which both reaction centres are located in the same molecule also enter into the diene synthesis. Thus intramolecular cyclisation with formation of phthalanes takes place on heat treatment of the propargyl ethers of vinyl- and isopropenyl-acetylenic alcohols[63]:



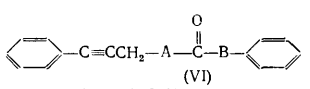
C_{sp}-Substituted propargyl ethers of vinylacetylenic alcohols also cyclise under analogous conditions[64]. The nature of the substituent in the acetylenic group has a significant influence on the reaction[65]. Electron-accepting groups facilitate cyclisation, while electron-donating groups greatly hinder it. Copper chloride has been used as a catalyst in order to accelerate the diene concentration[66]. The role of the catalyst apparently consists in the formation of the ethynyl carbanion:



It is noteworthy that the intramolecular condensation of the propargyl ethers of phenylacetylenic alcohols proceeds under more severe conditions than that of their vinylacetylenic analogues[67]. The diene synthesis involving β,γ-dichloro-γ-phenylallyl(propargyl)ammonium halide salts in the presence of alkalis proceeds with elimination of HCl and leads to benzoindolinium derivatives in high yields[68]:



Alkenylphenylallylammonium salts undergo the diene condensation also in the absence of alkalis. The intramolecular 1,4-cycloaddition of propargyl compounds of type (VI) in the presence of acetic anhydride opens a new pathway to synthetic lignan lactones[69–72]:

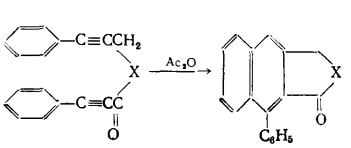


(VI)

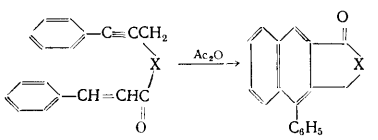
A=O, NH, $NCH_2C_6H_5$

B= *cis*-CH=CH, *trans*-CH=CH, C≡C .

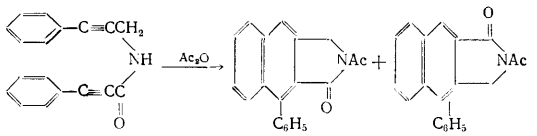
Here there is a possibility of the following pathways in the 1,4-cycloaddition: (1) electron-donating dienes interact with electron-accepting dienophiles (normal reaction); (2) electron-accepting dienes interact with electron-donating dienophiles (anomalous reaction). In the reaction of *N*-benzyldiynamide[70] and a diyne ester[69] the first pathway operates:



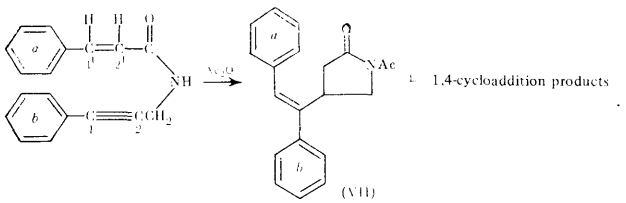
The intramolecular cycloaddition of *cis*- and *trans*-enynamides[71] and also of *N*-benzyl-*trans*-enynamide[70] proceeds via the second pathway:



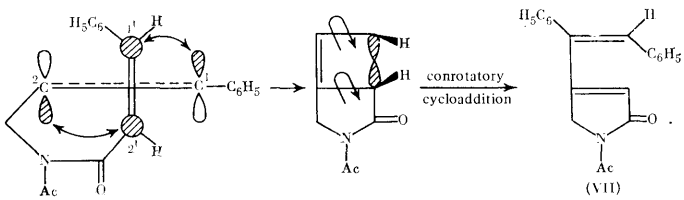
In the case of diynamides both pathways operate[71]:



There exist data[72] showing that, together with 1,4-cycloaddition products, yet another compound [compound (VII)] is formed in the intramolecular condensation of N-phenylpropargylamide of *cis*-cinnamic acid in the presence of acetic anhydride:

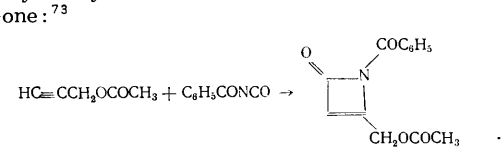


The use of deutero- and bromo-substituted analogues shows that compound (VII) is obtained as a result of the total rupture of the bond between the C(1′) and C(2′) atoms with formation of new C(1)–C(1′) and C(2)–C(2′) bonds. It has been suggested that this reaction takes place as a result of the thermally induced intramolecular concerted $[{}_{\pi}2_{s} + {}_{\pi}2_{a}]$-cycloaddition with formation of the sterically strained cyclobutene and subsequent conrotatory cyclodecomposition of the cyclobutene via the $[{}_{\sigma}2_{a} + {}_{\pi}2_{s}]$- or $[{}_{\sigma}2_{s} + {}_{\pi}2_{a}]$-mechanism. New bonds are formed in the suprafacial addition to the *cis*-C=C bond and the antarafacial addition to the C≡C bond. These bonds exhibit electron-donating and electron-accepting properties respectively:



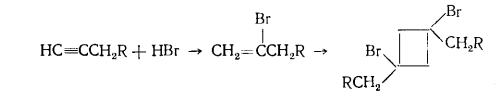
3. 1,2-Cycloaddition

The 1,2-cycloaddition to propargyl compounds has been studied inadequately. The interaction of propargyl acetate with benzoyl isocyanates leads to a substituted 1-benzoyl-2-azetin-4-one:[73]



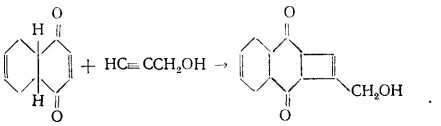
The cycloaddition of methyl propargyl ether to trichloroacetyl and benzoyl isocyanate has been considered in reviews[74,75].

The formation of cyclobutane derivatives from compounds of the type $HC{\equiv}CCH_2R$ in the presence of anhydrous HBr has been observed recently[76]. Together with the usual addition products, *cis*- and *trans*-1,3-dialkyl-1,3-dibromocyclobutanes are formed under these conditions (as a result of cyclodimerisation):



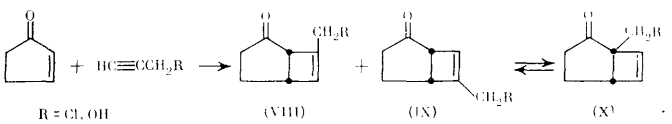
By varying the reaction conditions and the substituents R, it is possible to obtain cycloaddition products with maximum yields.

The photocycloaddition of a Δ^2-ene-1,4-dione to propargyl alcohol ($\lambda > 300$ nm) in benzene at room temperature leads to adducts of the tricyclo[6.4.0.$0^{3,6}$]dodecane series containing the cyclobutene ring[77]:



Under the same conditions, cyclopent-2-ene-1,4-diones do not form such rings owing to their extremely high tendency towards photopolymerisation. However, by altering the reaction conditions, it is possible to achieve the cycloaddition of propargyl alcohol in this case also[77].

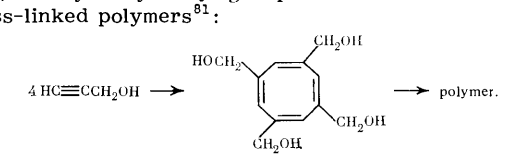
In order to elucidate the influence of the nature of the substituent in propargyl compounds on the ease and structural specificity of the cycloaddition, the photocycloaddition of cyclopent-2-en-1-one to propargyl chloride and propargyl alcohol has been investigated[78,79]:



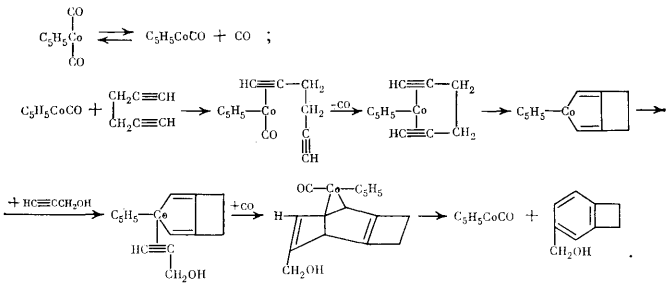
The reaction of cyclopentenone with propargyl chloride in ether proceeds comparatively unambiguously. Only the "head-to-head" and "head-to-tail" adducts, compounds (VIII) and (IX) respectively, are formed at the beginning of the photolysis in proportions of 3:1, after which their photoisomerisation products (X) appear. At the end of the photolysis the product of the addition of the solvent to cyclopentenone also accumulates. The reaction of propargyl alcohol with cyclopentenone in benzene is slow and compounds (VIII) and (IX) obtained initially undergo photopolymerisation with formation of minor products having a labile structure. It has been established that the structural specificity of the cycloaddition of cyclopentenone to propargyl compounds depends greatly on steric factors.

Methoxymethyl-3,4-carbonyldioxycyclobutene is formed in 22% yield in the photocycloaddition of methyl propargyl ether to vinylene carbonate[75].

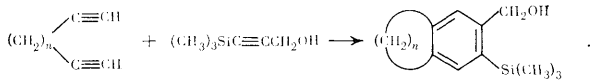
The cyclodimerisation, cyclotrimerisation, and cyclooligomerisation reactions also belong to the class of 1,2-cycloadditions. The direction of these reactions depends mainly on the type of catalyst employed. Thus cyclic trimers and tetramers have been synthesised from propargyl alcohols in the presence of di(π-allyl)nickel[80]. The cyclisation of propargyl alcohol catalysed by nickel acetylacetonate and its mixture with triphenylphosphine leads to 1,3,5,7-tetra-(hydroxymethyl)cyclo-octatetraenes. When the latter are heated, the hydroxymethyl groups condense with formation of cross-linked polymers[81]:



The most active catalysts in the intermolecular cycloaddition of propargyl compounds are transition metals[82,83]. The 1,2-cycloaddition process has been thoroughly investigated in relation to the interaction of propargyl alcohol with bipropargyl and its C_{sp}-substituted derivatives in the presence of Δ^5-cyclopentadienylcobalt dicarbonyl[84]. The results obtained[85,86] led to many well-founded hypotheses concerning the reaction mechanism which reduces, to the following scheme[84]:



The reaction of silicon-containing propargyl compounds with diacetylenes catalysed by $C_5H_5Co(CO)_2$ is an interesting type of cocyclisation[87–89]:



An increase in the length of the polymethylene chain favours cycloaddition.

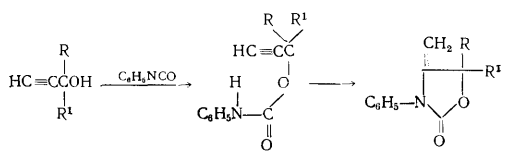
III. CYCLISATION

1. Intramolecular Addition to the Triple Bond

The cyclisation of propargyl compounds via intramolecular addition to the triple bond has found extensive applications in the synthesis of a wide variety of carbocyclic and heterocyclic systems. The rings are formed via the intramolecular addition of NH, OH, CH, SH, and ZH groups.

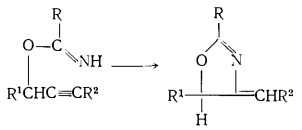
(a) NH-Addition

Five-membered heterocycles are synthesised by the intramolecular attack by the NH group on the C≡C bond. Thus the interaction of terminal propargyl alcohols with phenyl isocyanate leads initially to the corresponding carbamates, which readily undergo intramolecular cyclisation in the presence of bases and are converted into oxazolidinones[90–93]:



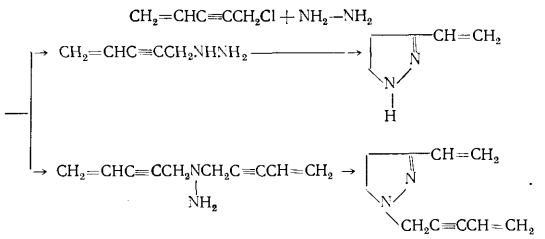
When the acetylenic hydrogen atom in the initial alcohol is replaced by bromine, bromo-oxazolidinones are formed, but, when the hydrogen is replaced by the aminomethyl group, the reaction cannot be carried out[93]. This difference in the behaviour of the aminoalcohol carbamates and their analogues can be explained by the polar influence of the C_{sp} substituent. Since heterocyclisation takes place as a result of the nucleophilic attack by the nitrogen atom of the carbamate group on the ethynyl carbon atom, the polarisation of the triple bond, generating a partial positive charge on the attacking atom, is essential for its successful occurrence.

On heating in benzene in the presence of 1,5-diazabicyclo-[5.4.0]undec-5-ene, propargyl benzimidates are converted into methyleneoxazolines in 45–50% yield[7]:

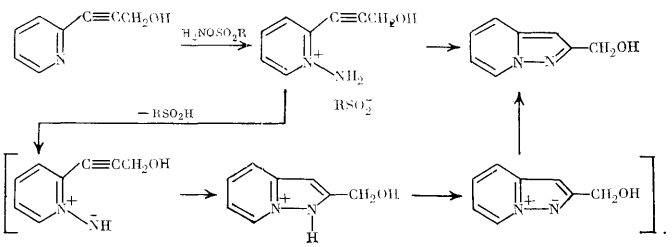


The latter are stable compounds. On treatment with t-C_4H_9OK, they are converted into oxazoles. The possibility of synthesising oxazole derivatives in the presence of Ag^+ or Hg^+ salts in 97.3% yield has been demonstrated recently[94].

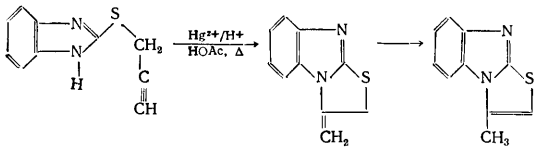
When hydrazine or phenylhydrazine reacts with primary vinylpropargyl halides in the presence of CuCl, substitution products are formed and then cyclise to vinylpyrazolines[95–98]:



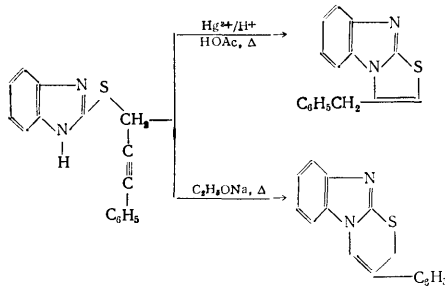
Tertiary vinylpropargyl halides and propargyl halides behave analogously in reactions with hydrazine. However, secondary vinylpropargyl halides do not give rise to pyrazolines, which are formed as a result of the direct attack by the nucleophile on the carbon atom linked to the halogen and subsequent cyclisation of the hydrazine formed. C_{sp}-pyridylpropargyl alcohol reacts with *O*-mesitylenesulphonylhydroxylamine to form the corresponding salt which is converted into pyrazolopyridine in 70–90% yield on treatment with potassium carbonate in dimethylformamide (DMF).[99] The similar transformation of propargylammonium compounds of the type $\diagdown\overset{+}{N}-CH_2C\equiv CH$ usually proceeds via a 2,3-sigmatropic rearrangement[100–102]. The explanation of the conversion of C_{sp}-pyridylpropargyl alcohol into pyrazolopyridine in terms of the formation of an allene intermediate is unconvincing, since it is difficult to assume the possibility of the formation of a strained five-membered cyclic compound with an allene group. It has been suggested[99] that the attack by NH on the electrophilic centre of the triple bond results in the formation of a dipolar ion which is stabilised as a consequence of the migration of hydrogen:



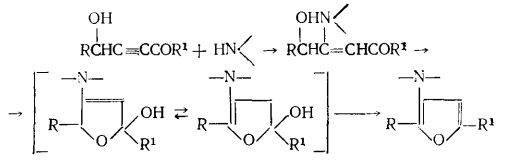
Terminal propargylthiobenzimidazoles give rise to satisfactory yields of 3-methylthiazolo[3,2-*a*]benzimidazoles in the presence of mercury ions[103]:



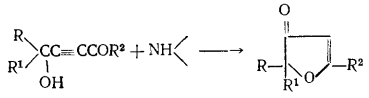
The cyclisation of C_{sp}-substituted propargylthiobenzimidazoles gives rise to 3-benzylthiazolo[3,2-*a*]benzimidazoles or 4-phenyldihydrothiazino[3,2-*a*]benzimidazoles depending on the reaction conditions[103]:



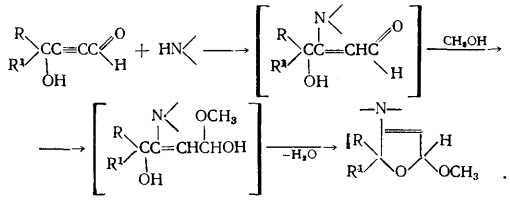
Certain reactions involving the addition of amines to propargyl compounds are accompanied by cyclisation. Thus the interaction of secondary propargyl ketols with primary and secondary amines leads to the formation of β-aminofurans[104,105]:



It has been suggested that nucleophilic addition of the amine to the triple bond takes place initially with subsequent cyclisation of the resulting aminovinylketol to β-aminofuran. Tertiary γ-ketols are converted into β-furanones on treatment with secondary amines and subsequent hydrolysis[106]:

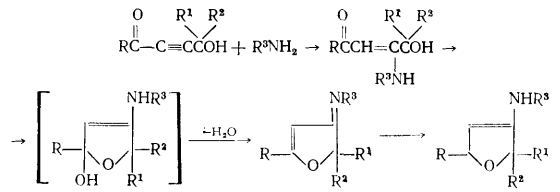


Propargylaldols react with primary amines to form acyclic compounds[107]. The attempts to achieve the nucleophilic addition of diethylamine to propargylketols in anhydrous media [ether, tetrahydrofuran (THF), and benzene] lead to tarry products[108]. Propargylaldols combine with dialkylamines in anhydrous methanol and are converted into stable 4-dialkylamino-2-methoxydihydrofurans in 43–54% yield. The solvent as well as the dialkylamine apparently adds on in this instance[108]:

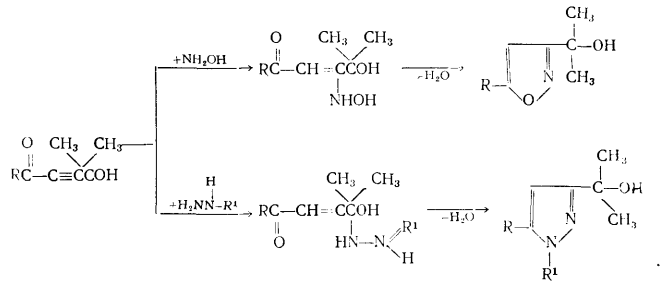


In absolute benzene or ether in an argon atmosphere the addition of diethylamine is accompanied by charring and an individual product cannot be isolated.

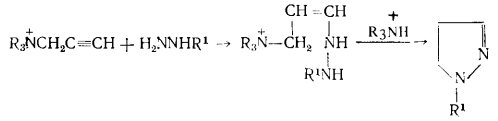
The addition of primary amines to propargylketols proceeds in accordance with the mechanism[109]:



The interaction of propargylketols with bifunctional nucleophiles (hydrazine, hydroxylamine) in a weakly alkaline medium involves the triple bond. The adducts formed initially cyclise to isoxazoles and pyrazoles[110]:

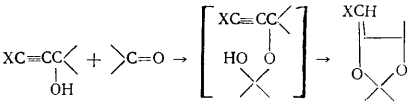


The reaction of hydrazine with trialkylpropargylammonium salts leads to the formation of pyrazolines[111]:



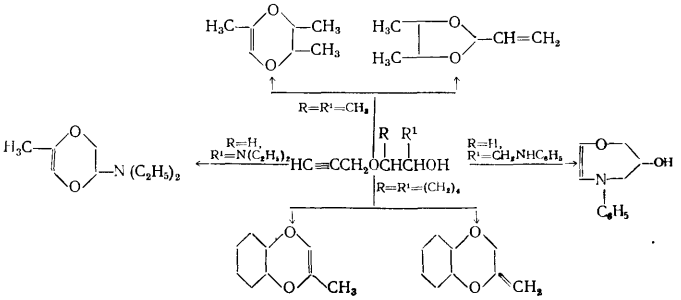
(b) OH-Addition

Among intramolecular cyclisations, the intramolecular addition of the OH group is of special interest. Thus it has been shown that, when propargyl alcohols interact with carbonyl compounds, substituted 1,3-dioxolans are formed[112–118]:

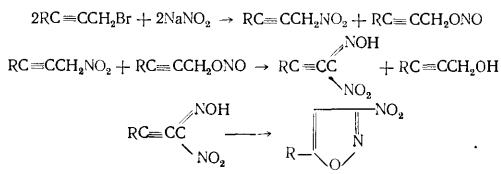


The extent and ease of cyclisation depend on the substituent X. The reaction proceeds readily when X = RC≡C, Br, RCOO, CN, or ROO.[117] On the other hand, the reaction does not occur at all when X = H, CH_2 = CH, C_6H_5O, CH_2OH, $CH(OC_2H_5)_2$, or CH_2OCH_3.[117,118] By comparing the spectroscopic characteristics of propargyl alcohols with their reactivities in the heterocyclisation reactions with carbonyl compounds, it has been established[117] that there is a qualitative relation between the reactivities of propargyl alcohols and the differences $\Delta\delta$ between the chemical shifts of the ≡CH group in the ^{1}H NMR spectra. Thus compounds for which $\Delta\delta$ is small are unreactive. Propargyl alcohols with functional group substituents which are actively involved in cyclisation have high values of $\Delta\delta$.

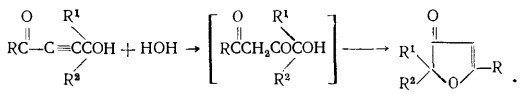
The cyclisation of alkyl-substituted propargyloxyethanols leads to rings of different size[119]:



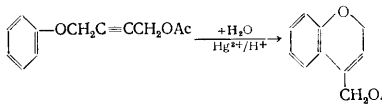
The application of propargyl compounds in the synthesis of isoxazole derivatives has been described[120]. Thus 3-nitroisoxazole has been obtained from propargyl bromide and sodium nitrite in DMF. The cyclisation of C_{sp}-substituted propargyl bromides also leads to 3-nitroisoxazoles[121]:



This mechanism has been confirmed by the isolation from the reaction mixture of a C_{sp}-substituted propargyl alcohol. In some cases the hydration of propargyl compounds also leads to the formation of rings. Propargylketols are fairly readily hydrated in dilute sulphuric acid or in alcoholic alkali in the presence of mercury salts and also in the presence of amines in protic solvents[104,122,123], being converted under these conditions into β-furanones, apparently via a β-diketol stage. In aqueous dioxan the yield of furanones is ≤50%:



Under analogous conditions, the C_{sp}-acetoxymethylpropargyl ether of phenol gives rise to 4-acetoxymethyl-Δ^3-chromene[124]:

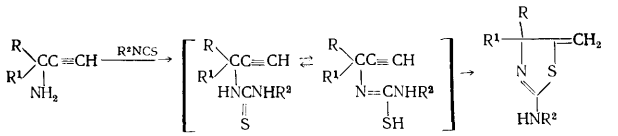


Under the same conditions, phenyl propargyl ether is converted into phenoxyacetone.

An interesting cyclisation of phenolic and enolic propargyl compounds has been discovered recently[125,126]. The monopropargyl ether of catechol is converted into 2,3-dihydro-2-methylene-1,4-benzodioxin in 65–90% yield on refluxing with mercury(II) oxide in DMF. In the absence of a catalyst and at temperatures below 110 °C, cyclisation does not occur. 2,3-Dihydro-2-methylenenaphtho[2,3-*b*]dioxin has been obtained under analogous conditions from the monopropargyl ether of 2,3-dihydroxynaphthalene.

(c) SH-Addition

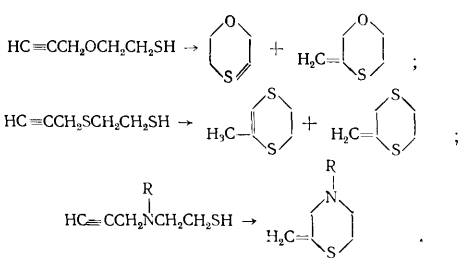
The intramolecular addition of the SH group to the C≡C bond is used to synthesise sulphur-containing heterocycles. There exists the view[127] that, when α,α-disubstituted propargylamines react with isothiocyanates, thiourea derivatives are formed initially and then give rise to the final reaction products under the influence of bases. However, Azerbaev et al.[128] believe that the intermediate thiourea derivatives are immediatley converted into thiazolines (via the thione–thiol tautomeric equilibrium):



Secondary α-propargylamines react with isothiocyanates to form thiazolidines. The reactions of isothiocyanates with secondary amines are slower than those with primary amines. It is noteworthy that cyclisation becomes more difficult with an increase in the bulk of the groups R^1 and R^2. The tendency towards cyclisation also diminishes with increase in the size of the group R. Similar features of the cyclisation had also been noted earlier[127,129] and the difficulties in the cyclisation reaction were accounted for by steric factors.

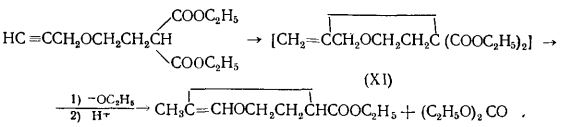
The interaction of α,α-disubstituted propargylamines with benzoyl isothiocyanate leads the formation of 2-benzamido-5-methylene-2-thiazoline[130]. It has recently been suggested[131] that the interaction of aryl isoselenocyanates with 2-alkynylamines proceeds analogously to the reaction with isothiocyanates, i.e. via the intermediate formation of seneloureas which undergo cyclisation during the reaction with formation of the corresponding selenazolines. The reactions of 2-propynylamines with isoselenocyanates proceed more vigorously than those with isothiocyanates.

Compounds containing heteroatoms between the thiol and propargyl groups can also be used to synthesise heterocycles. It has been established[132] that the structure of the products of the cyclisation of propargyl derivatives of hydroxy-, mercapto-, and amino-ethanethiols in the presence of bases depends on the nature of the heteroatom. Whereas a mixture of 2-methylene-1-thia-4-oxacyclohexane and 3-thia-6-oxacycloheptene is formed from propargyloxyethanethiol, in the reaction involving propargylthioethanethiol the main reaction products are 2-methylene-1,4-dithia-2-cyclohexene and 2-methylene-1,4-dithiacyclohexane. Only one cyclic product, namely 2-methylene-1-thia-4-azacyclohexane, is formed from propargylaminoethanethiol:



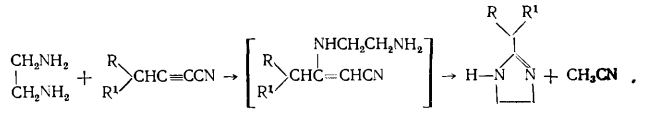
(d) CH-Addition

Propargyl compounds containing an active hydrogen atom undergo the Michael reaction with formation of cyclic compounds. Thus the intramolecular cyclisation of propargyloxyethylmalonic ester in the presence of sodium ethoxide in alcohol leads to derivatives of dihydropyran[133]:

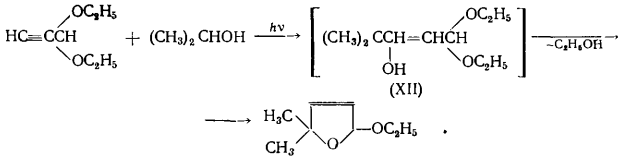


It has been suggested that the intermediate compound (XI) interacts with the ethoxide anion, splits off diethyl carbonate, and is converted into the final product.

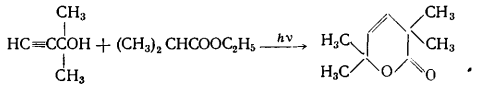
The Michael adducts of ethylenediamine and the "inverted" propargyl cyanides readily cyclise to imidazolines (yield 80%) with elimination of acetonitrile[134]:



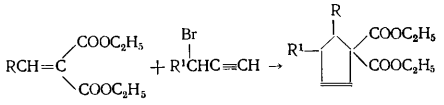
The photochemical reaction of the diethyl acetal of propiolaldehyde with isopropyl alcohol proceeds via the intermediate (XII) and gives rise to a dihydrofuran derivative as a result of the elimination of ethanol[135]:



Under these conditions, propargyl alcohols are converted into acyclic compounds[136]. The interaction of ethynyldimethylmethanol with ethyl isobutyrate results in the formation of a pyrone derivative[137]:

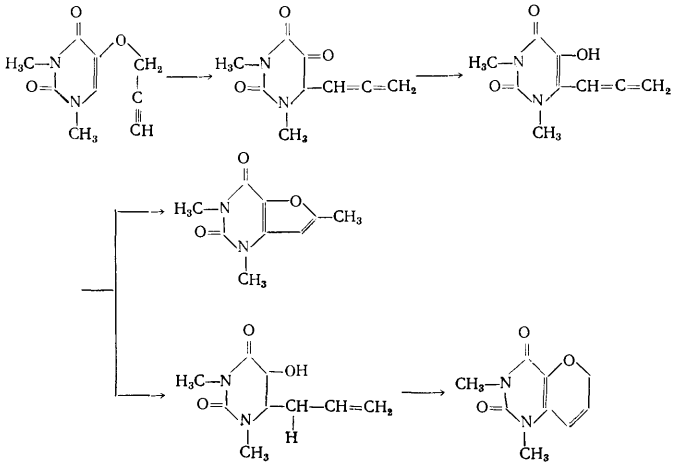


The addition of diethyl isobutylidenemalonate to secondary propargyl bromides in the presence of zinc or on heating in THF can be regarded as a new method of synthesis of cyclopentene derivatives[138]:

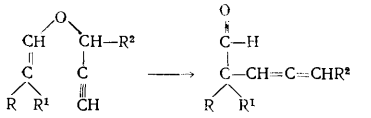


2. Cyclisation Involving the Claisen Rearrangement

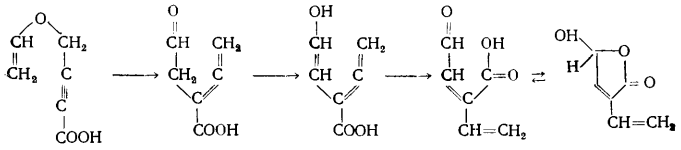
One of the commonest methods of synthesis of heterocycles involves the cyclisation of propargyl compounds via a sigmatropic rearrangement. Thus the thermal cyclisation of propargyl ethers of phenols leads to the formation of chromenes[75]. In contrast to this, the cyclisation of propargyloxyuracils results in the additional formation of furopyrimidine[2]:



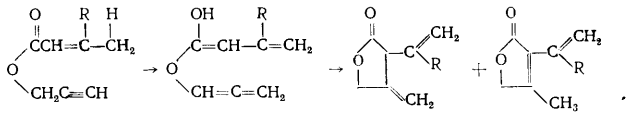
This can be explained by the fact that the electron-withdrawing effect of the uracil nucleus is greater than that of the phenyl group. This effect renders the central carbon atom of the allene fragment in the enol more electron deficient. As a consequence of this, the sensitivity of the enolic hydroxy-group to nucleophilic attack increases and ring closure results. The solvent exerts a decisive influence on the mode of cyclisation. Furopyrimidines (66%) are formed from substituted propargyloxyuracils in DMF at 130 °C. Pyrolysis in xylene at 130 °C leads to pyranopyrimidines (48%). The propargyl ethers of hydroxymethylacridone[4], substituted hydroxynapthalenes[3], coumarins[139–141], and hydroquinone[142] behave analogously in the intramolecular cyclisation reaction. Propargyl vinyl ethers react differently. Their thermal cyclisation with a vinyl fragment containing vinyl substituents leads to allenyl-substituted aldehydes[143]:



The cyclisation of the C_{sp}-carboxyether leads to the formation of a natural antibiotic—the lactone of dihydroxyvinylbutanoic acid[5]:

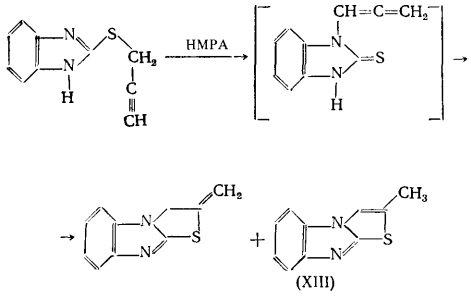


It has been suggested that the initial propargyl vinyl ether is converted via a cyclic transition state into an allene aldehyde, which undergoes a prototropic rearrangement with formation of a diene aldehyde which then cyclises to the final product. Alkenyl-γ-lactams and alkenyl-γ-lactones have been obtained from propargylamides or propargyl esters of alkanoic acids[144–146]. The reaction mechanism is as follows:

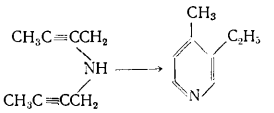


The unsaturated ester of the propargyl alcohol probably enolises with participation of an α-hydrogen atom as a result of 1,5-migration with formation of an intermediate, which is converted into the final product via the mechanism of the ene reaction involving the transfer of a hydrogen atom from the enol group.

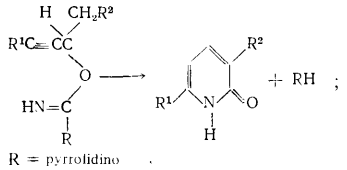
An instant rearrangement has been observed in the thermal cyclisation of propargylthiobenzimidazole in hexamethylphosphoramide (HMPA):[147,148]



Only compound (XIII) is formed in ethanol in the presence of sodium ethoxide. Under these conditions, dipropargyl sulphides do not cyclise. The thermal rearrangement of C_{sp}-alkyl-substituted dipropargylamines in the presence of potassium t-butoxide in butyl alcohol leads to alkylpyridines[149]:



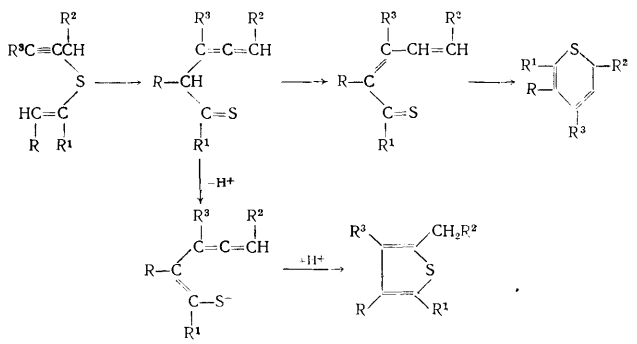
Under these conditions, the unsubstituted dipropargylamine is converted into the corresponding nitrile. A new method of synthesis of 2-pyridones by the thermolysis of *O*-propargyl derivatives of isoureas has been described[150,151]:



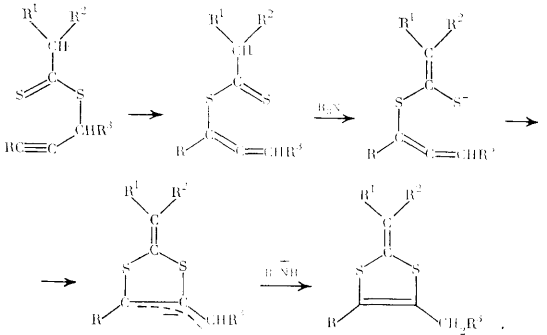
R = pyrrolidino

It has been suggested that the initial reaction stage is the thermal 3,3-sigmatropic rearrangement of the initial compound into an allene, whose tautomeric transformation gives rise to the corresponding diene. The elimination of pyrrolidine from the diene leads subsequently to an isocyanatodiene, which undergoes electrocyclic cyclisation to a pyridone.

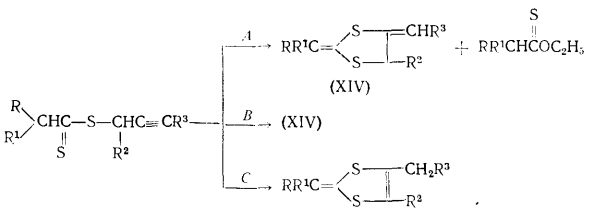
Sulphur-containing vinylpropargyl compounds also undergo the Claisen rearrangement[152,153]. An allene intermediate is formed in the initial stage. Its subsequent transformation can take place with formation of various substituted heterocycles:



The solvent and the presence of an amine exert the most significant influence on the direction of the reaction. The reaction in HMPA leads to the specific synthesis of 2*H*-thiopyrans. The basicity of HMPA apparently favours the 1,3-isomerisation of the allene intermediate to a conjugated diene, whose subsequent transformation leads to a thiopyran. When the reaction is carried out in HMPA or dimethyl sulphoxide (DMSO) in the presence of amines, mixtures of substituted thiopyrans and thiophens are formed. Amines probably catalyse the conversion of the allene intermediate into a thiophen. Propargyl vinyl sulphides containing the cyano-group in the vinyl fragment gives rise to thiopyrans on heating in silicone oil, while in DMSO in the presence of di-isopropylamine they produce a mixture of thiopyran and thiophens[154]. Propargylthiothiopyran cyclises like propargyl sulphides with formation of thiopyranothiopyran and thiopyranothiophen[155]. The thermal cyclisation of propargyl alkanedithioates in xylene proceeds via the mechanism[156]



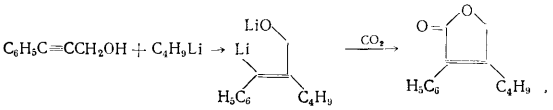
The base-catalysed cyclisation of propargyl alkanedithioates has been investigated[157]. The reaction can be carried out in the presence of sodium ethoxide in absolute alcohol (method *A*) or in the presence of potassium t-butoxide in a mixture of t-butyl alcohol and the dimethyl ether of ethylene glycol (method *B*) and also in the presence of sodium ethoxide or potassium t-butoxide in the dry dimethyl ether of ethylene glycol (method *C*):



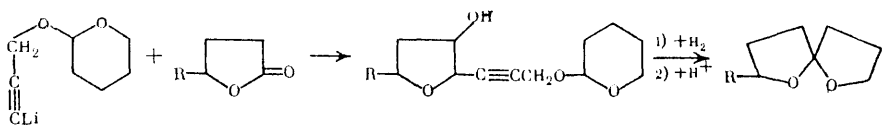
3. Other Cyclisation Reactions

Apart from the reactions described, a number of non-general cyclisation reactions have been described for propargyl compounds.

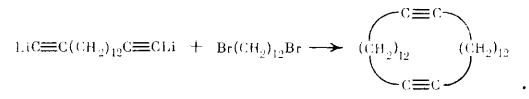
C_{sp}-phenyl-substituted propargyl alcohol readily reacts with butyl-lithium in ether in the presence of symmetrical *N*,*N*'-dimethylethylenediamine to form an intermediate whose reaction with carbon dioxide leads to the corresponding lactone in a yield up to 70%:[158]



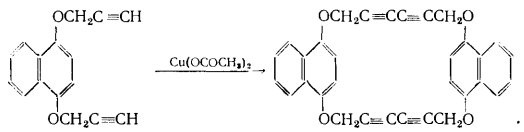
C_{sp}-Lithio-derivatives of propargyl ethers react with lactones in diethyl ether and give rise to hydroxylactones whose hydrogenation and subsequent acid hydrolysis afford the corresponding spiro-compounds[159]:



The dilithio-derivative of hexadeca-1,10-diyne is readily alkylated by 1,12-dibromododecane in a THF–HMPA mixture with formation of a 28-membered macrocycloalkadiyne[160]:

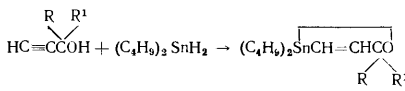


The intermolecular cyclisation of 1,4-dipropargyloxynaphthalene in the presence of copper acetate on heating in pyridine has been reported recently[161]. The reaction leads to the formation of a tetrayne crown-ether in 96% yield:



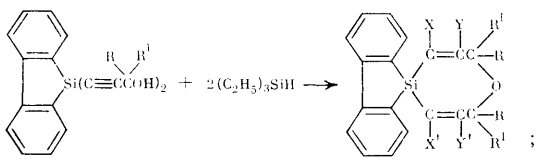
Other propargyl ethers have also been introduced into this reaction[162].

The interaction of dibutylstannane with propargyl alcohols leads to unsaturated cyclic organotin ethers[163]:



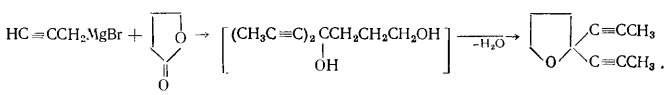
The addition of dialkylchlorohydrosilanes and the corresponding germanes and stannanes to substituted propargyl alcohols gives rise to the corresponding γ-hydroxyalkenyl analogues. The reduction of the latter with lithium tetrahydroaluminate and subsequent intramolecular dehydrocondensation led to the synthesis of 2-sila-, 2-germa, and 2-stanna-1-oxacyclopentanes[164]. The ease of cyclisation depends on the polarity of the metal–hydrogen bond.

Iotsich reagents derived from propargyl alcohols react with dichlorosilafluorene to form silicon-containing glycols whose hydrosilylation with triethylsilane is accompanied by cyclodehydration[165]:

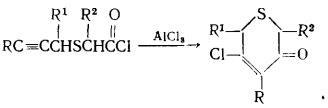


X, Y, X', Y' = $(C_2H_5)_3Si$ or H .

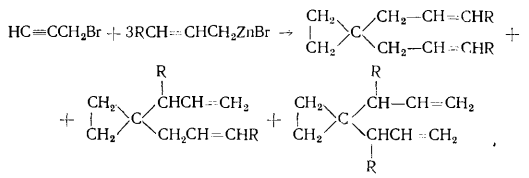
There exists the view that the final product of the interaction of the Grignard reagent derived from propargyl bromide with γ-butyrolactone, namely 2,2-dipropynyltetrahydrofuran, is also formed via the cyclodehydration of the intermediate 1,4-diol:[166]



The intramolecular cyclisation of chlorides of propargylthioalkanecarboxylic acids catalysed by $AlCl_3$ leads to derivatives of dihydrothiopyranones[167]:



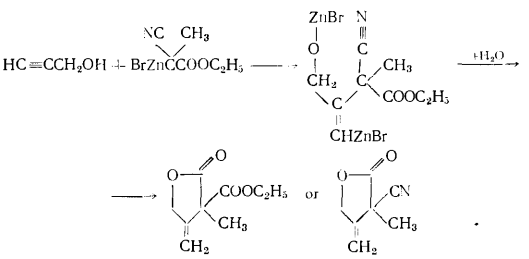
The addition of unsaturated organozinc compounds to the propargyl compounds $HC{\equiv}CCH_2X$ leads either to the normal adducts or to cyclic compounds[168–170]. The reactions of propargyl alcohols (X = OH), ethers (X = OR), and their nitrogen-containing analogues (X = NR_2) result in the formation of mono- or di-addition products. Only diaddition takes place in the reaction of propargyl bromide or chloride with subsequent 1,3-elimination and the formation of cyclopropane derivatives. When propargyl bromide is treated with substituted allyl derivatives of organozinc compounds, mixtures of three substituted cyclopropanes are produced:



The lotsich reagent derived from phenyl propargyl ether reacts with C_{sp}-ethyl-substituted propargylzinc bromide, also forming a cyclopropane derivative[171]. In contrast to this, the formation of acyclic compounds is observed in the reaction of propargyl alcohol with the lotsich reagent.

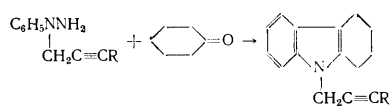
Treatment of propargyl bromide with organomagnesium compounds results in the formation of the products of the Wurtz exchange reaction and also the products of an intramolecular rearrangement[172–174].

The reaction of propargyl alcohol with the zinc derivative of ethyl bromocyanopropionate leads to the formation of γ-lactones[175,176]:

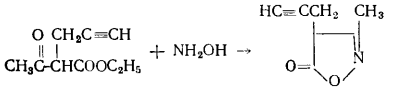


Mixtures consisting of lactones, adducts, and transesterification products are formed from secondary propargyl alcohols. The reaction involving tertiary propargyl alcohols affords a complex mixture of products Under these conditions, C_{sp}-substituted propargyl alcohols do not react and diethylpropargylamine gives rise to addition products alone.

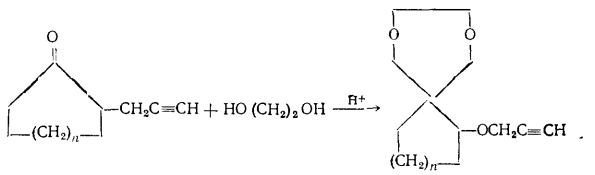
Certain cyclisation reactions of propargyl compounds proceed without involving the triple bond. This permits the specific use of the latter in subsequent reactions. Propargylphenylhydrazines are readily converted into *N*-propargyltetrahydrocarbazoles on interaction with cyclohexanone in acetic acid[177]:



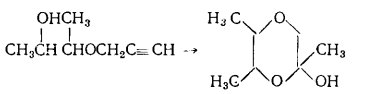
The propargyl group is retained also in the intermolecular cyclisation of ethyl propargylacetoacetate with hydroxylamine[178]:



2-Propargylcycloanones react with glycol to form the corresponding propargyl spirodioxolans[179]:



The monopropargyl ether of butane-2,3-diol undergoes cyclohydration in an aqueous medium in the presence of mercury(II) oxide and sulphuric acid with formation of 2-hydroxy-2,5,6-trimethyl-1,4-dioxan[180]:



The interaction of propargyl alcohols with the β-chloroalkyl ethers of glycidol in the presence of $BF_3.(C_2H_5)_2O$ leads to the formation of derivatives of propargyloxymethyl-1,4-dioxan[181].

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Nesmeyanov Institute of Organoelemental Compounds,
USSR Academy of Sciences, Moscow

Azizbekov Azerbaijan Institute of Petroleum and Chemistry, Baku

Translated from *Uspekhi Khimii*, 53, 880-895 (1984) U.D.C. 541.64 : [illegible]39.199 : 532.72

Dynamic Light Scattering and Thermal Motion of Macromolecules in Solutions

V.S.Skazka

The theory and practice of a new method of studying the translational and rotational mobility of macromolecules in solution by dynamic light scattering are briefly outlined. Experimental assemblies are described, and results obtained by this method for macromolecules of different chemical structure are reported. The possible applications of the method and its likely future developments are discussed.
The bibliography includes 47 references.

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I. INTRODUCTION

In diffusion, sedimentation, and viscosity phenomena the organised translational and rotational motion of macromolecules in solutions takes place as a result of their interaction with an external field of force: in diffusion, the field of the chemical potential gradient, in sedimentation, the centrifugal force field, and in viscous flow, the field of the flow velocity gradient. The presence of these fields (external to the macromolecule) can perturb the results. Therefore in many experiments allowance must be made for these perturbing effects, usually by extrapolating the results to zero values of the fields or gradients.

However, we can approach the study of the mobility of macromolecules in a different way: by using the dynamic light scattering method. Macromolecules in solution are in a state of continuous thermal motion. The displacement of their centre of gravity, which characterises the "macro-Brownian" motion[1], can be described according to Einstein's theory in terms of the translational diffusion coefficient D. The "micro-Brownian" motion of the individual segments of the macromolecule is determined by the rotational diffusion coefficient D_r and by the spectrum of relaxation times for the small-scale intramolecular motions[2]. The Brownian motion causes fluctuations in the concentration of the macromolecules in solution, and these fluctuations can scatter the electromagnetic energy when a light wave is passed through the solution. Therefore the light scattered by a solution of a polymer must contain (in principle) information on the kinetic characteristics of the macromolecules.

II. THEORETICAL FOUNDATIONS

The classical theory[3] deals with the scattering of light on time-averaged fluctuations of the concentration of the solution $\overline{(\Delta c)^2}$. This treatment leads to formulae giving the molecular weight of the dissolved macromolecules, their size, and the thermodynamic parameters of the solution–solvent system from the intensity of the scattered light[3].

In practice, however, the fluctuations are time-dependent owing to the presence of thermal Brownian motion, and therefore the time dependence of the fluctuations is determined by the kinetic parameters of the macromolecules in solution. Concentration fluctuations arise, grow, and disappear with time: this produces a modulation of the frequency of the scattered light, i.e. a shift of its frequency with respect to the incident frequency. The frequency shift can be interpreted as the manifestation of the Doppler effect during light scattering by moving macromolecules whose velocity in the solution is determined by the intensity of the Brownian motion. The light scattered by the solution will have a distribution of frequency (of variable width) with a profile centred on frequency of the incident light. Thus the width of the scattering spectrum carries information on the statistical distribution of the kinetic parameters of the macromolecules in solution.

The molecular theory of the spectral distribution of the intensity of light scattered by liquids was formulated by Komarov and Fisher[4], who used the mathematical framework of space–time correlation functions proposed by van Hove[5]. For any system of N particles we can define the probability density G_1 of finding a given particle at time $t = 0$ at a point in the solution having the coordinate r_0, and at time $t > 0$ at the point r, irrespectively of the position of the other particles. Another characteristic quantity (G_2) defines the probability density of finding a particle at the point r in the solvent at time $t > 0$ when another particle is at the point r_0 at time $t = 0$.

The functions G_1 and G_2 are the internal and the external autocorrelation function respectively. The internal autocorrelation function G_1 describes the probability of displacements of a given particle in the solution, the external function G_2 describes the probability of the relative displacement in the solution of two particles whose motions are assumed to be mutually independent.

The time autocorrelation function $G(\tau)$ for any function $x(t)$ is given by the expression

$$G(\tau) = \lim_{T\to\infty} \frac{1}{2T} \int_{-T}^{T} x(t)\, x^*(t+\tau)\, \mathrm{d}t = \langle x(t)\, x^*(t+\tau) \rangle ,$$

where $x(t)$ is the value of the function at time t, and $x^*(t + \tau)$ is the complex conjugate value of this function at time $t + \tau$: the angle brackets denote averaging with respect to time. The autocorrelation function differs from other averages in being independent of the variable τ.

The spectral density of the intensity of scattered light is found by a Fourier transformation of the space–time function for the scattering system:

$$\mathcal{J}(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(i\omega\tau)\, d\tau .$$

The theory of dynamic light scattering by solutions of polymers was developed by Pecora[6–8]. The theory is too complex to be reviewed in detail, and we shall confine ourselves to describing the main physical postulates on which it is based. Pecora considers two independent correlation functions. The first [the autocorrelation functions for the centre of gravity of the macromolecule, $G_\phi(\tau, \mathbf{r})$] is defined as the probability of finding the centre of gravity of a molecule at the point r at time $t > 0$ if at time $t = 0$ the centre of gravity of the same molecule is at the origin of the coordinate system. The second correlation function is the space–time correlation function $G_A(\tau, \mathbf{r})$, which defines the probability of a second segment of a macrmolecule being found at the point r at time $t > 0$ if an arbitrarily chosen segment of the same macromolecule is at the origin at time $t = 0$. Thus the quantity $G_A(\tau, \mathbf{r})$ defines the correlation between the motions of the segments within the macromolecule.

The optical spectrum of the scattered light is found by Fourier transformation of the correlation functions $G_\phi(\tau, \mathbf{r})$ and $G_A(\tau, \mathbf{r})$:[9]

$$\mathcal{J}(\omega) = \frac{N}{2\pi} \int_{-\infty}^{\infty} G_A(\tau, \mathbf{r})\, G_\Phi(\tau, \mathbf{r}) \exp[i(\omega - \omega_0)\tau]\, d\tau ,$$

where

$$G_A(\tau, \mathbf{r}) = \langle A(t) A^*(t+\tau) \rangle$$
$$G_\Phi(\tau, \mathbf{r}) = \langle \exp\{-i[\mathbf{q}, \mathbf{r}(t)]\} \exp\{i[\mathbf{q}, \mathbf{r}(t+\tau)]\} \rangle .$$

The vector q is the difference between the wave vectors of the incident and the scattered wave. Its numerical value is

$$q = \frac{4\pi n_0}{\lambda_0} \sin\frac{\vartheta}{2} .$$

In this expression n_0 is the refractive index of the medium, λ_0 is the wavelength of the incident light in a vacuum, and ϑ is the scattering angle.

The physical meaning of the quantity $A(t)$ can be explained as follows. The light wave scattered by every jth particle (of a total number N of particles) is defined by the equation

$$E_j = A_j(t) \exp\{-i[\mathbf{q}, \mathbf{r}_j]\} \exp(i\omega_0 t) ,$$

where $A_j(t)$ is the amplitude of the wave scattered from the jth particle.

The aggregate field of the light wave from N scattering elements is

$$E_s = \sum_{j=1}^{N} E_j = \sum_{j=1}^{N} A_j(t) \exp\{-i[\mathbf{q}, \mathbf{r}_j(t)]\} \exp(i\omega t) . \qquad (1)$$

The intensity of the scattered light is proportional to the square of the amplitude of the light wave:

$$\mathcal{J}_s = \langle |E_s|^2 \rangle , \qquad (2)$$

On the assumption that the light scattering events from all the particles in solution are mutually independent, carrying out the summation of Eqn.(2) after inserting Eqn.(1) into it gives

$$\mathcal{J}_s = \left\langle \sum_{j=1}^{N} |A_j|^2 \right\rangle = N \langle |A|^2 \rangle .$$

Thus the parameter $A(t)$ is the average amplitude of the scattered light wave.

If we ignore the intramolecular thermal motion of the macromolecules, i.e. if we neglect the rotational motion and the mutual displacement of the segments, the autocorrelation function takes it simplest form:

$$G_A(\tau, \mathbf{r}) = N |A|^2 .$$

The optical spectrum is given by the equation

$$\mathcal{J}(\omega) = N |A|^2 \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp[i(\omega - \omega_0)\tau]\, G_\Phi(\tau)\, d\tau .$$

The autocorrelation function $G_\phi(\tau)$ can be calculated by noting that it describes a time dependence analogous to that of a large concentration fluctuation artificially imposed on the system at time $t = 0$.[10] Concentration changes in such a fluctuation obey Fick's law, which for $G_\phi(\tau)$ can be written as

$$\partial G_\varphi(\tau)/\partial\tau = D\nabla^2 G_\varphi(\tau) , \qquad (3)$$

where D is the translational diffusion coefficient of the macromolecule. Solving Eqn.(3) by the method of Fourier transforms in space gives

$$G_\varphi(\tau) = \exp(-Dq^2\tau) . \qquad (3')$$

Hence

$$\mathcal{J}(\omega) = \frac{N|A|^2}{2\pi} \int_{-\infty}^{\infty} \exp[i(\omega - \omega_0)\tau] \exp(-Dq^2\tau)\, d\tau =$$
$$= \frac{N|A|^2}{2\pi} \frac{q^2 D}{(\omega - \omega_0)^2 + (q^2 D)^2} . \qquad (4)$$

The shape of the spectral line is Lorentzian, centred on the frequency ω_0. The half-width of the Lorentz outline, $(\Delta\omega)_{1/2} = (\omega - \omega_0)_{1/2}$, is simply related to the translational diffusion coefficient:

$$(\Delta\omega)_{1/2} = q^2 D . \qquad (5)$$

Usually in dynamic light scattering experiments the solution is irradiated with polarised light, with the electric vector of the light wave in a vertical plane, and the intensity of the scattered light with the same polarisation is measured. The intensity of this component can be denoted $\mathcal{J}_{VV}$, and identified with the the quantity given by Eqn.(4). It is also possible to determine the intensity of the component of the scattered light in which the polarisation of the light wave is horizontal ($\mathcal{J}_{HV}$).

Formula (4) applies if the size of the macromolecule $(\overline{h^2})^{1/2}$ is much less than the wavelength λ_0 of the incident light. The criterion of smallness for a molecule in dynamic light scattering is the same as the criterion adopted in the classical theory of light scattering[3]: $(\overline{h^2})^{1/2} \leq \frac{1}{20}\lambda_0$. Under these conditions the internal interference (Debye) function is $P(\theta) = 1$. For large molecules, when $P(\theta) < 1$, the intensity of the light scattered by isotropic spherical symmetrical molecules is obtained by multiplying the right-hand side of Eqn.(4) by $P(\theta)$.[8] In this case the $\mathcal{J}_{VV}(\omega)$ spectrum is unaffected by intramolecular motion.

On the other hand if the macromolecule is asymmetrical the scattering spectrum is affected by the internal thermal motion (molecular rotation). Assuming that the translational and the rotational motion of the macromolecule are mutually

independent we obtain the following equation for the spectrum of the scattered light:

$$\mathcal{I}_{vv}(\omega) = \frac{4NA}{\pi}\alpha^2\left\{\left|\frac{1}{n}\sum_{j=1}^{n/2}J_0(qb_j)\right|^2\frac{q^2D}{(\omega-\omega_0)^2+(q^2D)^2} + \right.$$
$$\left. + 5\left|\frac{1}{n}\sum_{j=1}^{n/2}J_2(qb_j)\right|^2\frac{q^2D+6D_r}{(\omega-\omega_0)^2+(q^2D+6D_r)^2} + \ldots\right\}. \qquad (6)$$

The scattered light spectrum is the sum of two Lorentzian curves whose relative statistical weight is determined by the squares of sums containing the spherical Bessel functions J_0 and J_2 (zero-order and second-order respectively). In Eqn.(6) n is the number of segments, b_j is the distance of the jth segment from the centre of gravity of the macromolecule, and α is the polarisability of the macromolecule.

The intramolecular Brownian thermal motion affects the spectral distribution of the intensity of scattered light. The micro-Brownian motion in a group of macromolecules has been calculated[11] by using the sub-chain model (see, for example, Ref.12), in which the macromolecule is assumed to contain a number of linearly arranged, freely interconnected segments, each of which acts as a flexible "sub-chain". The hydrodynamic interaction with the solvent is transmitted by beads at the ends of the sub-chains, which have a significant mass and a coefficient of friction ξ. Each bead experiences highly elastic forces from the neighbouring sub-chains. The action of these forces is similar to that of a spring with linear characteristics, and the distance between the ends of sub-chains is assumed to have a Gaussian distribution.

Thus by studying the dynamics of motion of the segments in real macromolecules we are studying the dynamics of motion of a set of beads interconnected by elastic springs and immersed in a viscous medium. The motion of the jth bead determines the jth mode of the intramolecular motion, and is characterised by a relaxation time (τ_j). Unfortunately the theory does not allow us to calculate τ_j for all j. Only τ_1 (which refers to the rotation of the macromolecule as a whole) is theoretically calculable. For the two extreme cases of negligibly small and of maximum possible hydrodynamic interaction (penetrable and impervious group of macromolecules respectively) the following formulae have been obtained[11] for τ_1:

$$\tau_1 = \frac{6M[\eta]\eta_0}{\pi^2RT} \text{ and } \tau_1 = \frac{0.422M[\eta]\eta_0}{\pi^2RT}.$$

The spectrum of the scattered light with allowance for the intramolecular thermal motion by the Rouse and Zimm theory is described by the equation[13]

$$\mathcal{I}_{vv} = P_0(x)\frac{q^2D}{(\omega-\omega_0)^2+(q^2D)^2} + \sum_{j=2}^{\infty}P_1(x)\frac{q^2D+1/\tau_j}{(\omega-\omega_0)^2+(q^2D+1/\tau_j)^2} +$$
$$+\sum_{j=1}^{\infty}P_2(x)\frac{q^2D+1/\tau_j}{(\omega-\omega_0)^2+(q^2D+1/\tau_j)^2}. \qquad (7)$$

The argument z of the scattered light amplitudes P_0, P_1, and P_2 depends on the size of the macromolecules: $x = q^2\bar{h}^2/6$. For $0 \leq x \leq 1$ the only contribution to $\mathcal{I}_{vv}(\omega)$ is that of the diffusional motion of the centre of gravity of the macrmolecules, given by the first term in the right-hand side of Eqn. (7). The contribution of the internal motion to the spectral distribution of the intensity of scattered light becomes significant only when $x \gg 1$. These values of x are reached only in macromolecules having a mass $>10^6$ and in measurements with large scattering angles θ.[14]

If the macromolecule has a significant optical anisotropy the spectral distribution of scattered light intensity shows contributions from the translational motion of the centre of gravity of the macromolecules (D) and from the rotation of the molecule as a whole, characterised by the rotational diffusion coefficient D_r. The rotation of the macromolecules modulates the intensity of the scattered light at a frequency equal to the rotation frequency of the group of macromolecules: this effect is directly observable in the spectrum of the scattered light. The intensities of the $\mathcal{I}_{vv}$ and $\mathcal{I}_{Hv}$ components in the scattered light are given by

$$\mathcal{I}_{vv}(\omega) = \frac{NA}{9\pi}(\alpha_\parallel + 2\alpha_\perp)^2\frac{q^2D}{(\omega-\omega_0)^2+(q^2D)^2} + \frac{4}{3}\mathcal{I}_{Hv} \qquad (8)$$

$$\mathcal{I}_{Hv}(\omega) = \frac{NA}{9\pi}(\alpha_\parallel - \alpha_\perp)^2\frac{q^2D+6D_r}{(\omega-\omega_0)^2+(q^2D+6D_r)^2}, \qquad (9)$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the polarisabilities of the macromolecules in directions parallel and perpendicular to the molecular axis respectively.

Eqns.(4), (6), (8), and (9) form the basis of all methods of determining D, D_r, and τ for macromolecules in solution from experimental measurements of the dynamic scattering of light.

In its present state of development the theory of the dynamic scattering of light does not allow for concentration effects in the system, i.e. it is strictly applicable only to solutions at infinite dilution. However, some experimental studies of the concentration dependence of the shape of the scattered line have been reported[15,16]. It is assumed implicitly that the equations which relate the shape of the spectrum to the parameters of the molecular motion remain valid at finite concentrations, but this assumption has no theoretical justification.

III. MEASUREMENTS PRINCIPLES

When using the dynamic light scattering method in practice we should note that the frequency shift of the scattered light for polymer solutions is of the order of $\Delta\omega \cong 10^3$–10^4 Hz. Therefore in order to distinguish these frequencies in the optical spectrum ($\omega_0 \cong 10^{15}$ Hz) we need a spectroscopic equipment with a resolving power of $\omega_0/\Delta\omega \cong 10^{11}$ or better. The resolving power of ordinary optical methods is far from being adequate for this purpose. Furthermore the spectral width of the incident light should be less than $\Delta\omega$: this condition can be met by using laser light.

The spectral distribution of the intensity of scattered light is studied by optical mixing methods, which are an extension to the optical frequency range of methods commonly used at radio frequencies[9,17]. The wanted signal is transmitted by using waves having a carrier frequency $\omega_0 \cong 10^6$ Hz, modulated at the frequency of the signal ($\Delta\omega$). In the detector these waves are mixed with a reference signal of frequency comparable to that of the carrier wave: the interference between the reference and the carrier frequency reveals the wanted signal $\Delta\omega$. By using a laser as the light source in conjunction with an FEU photoelectric amplifier and a spectrum analyser the same procedure can be applied to waves in the optical frequency range.

The optical mixing used in these measurements consists in the destructive interference of two light waves (reference, and carrier) incident on the cathode of the FEU. The result is a modulation of the current taken from the FEU. The modulation frequencies correspond to the frequencies in the wanted signal, and the signal is centred on the frequency difference between the reference wave and the information-carrying wave. If the frequency of the reference wave is comparable to that of the wave carrying the information (i.e. the light scattered by the polymer solution) the current taken from the FEU will display the frequencies of the wanted

signal. The dependence of the photocurrent on $\Delta\omega$ will be determined by the shape of the spectral line of the incident light, with the important difference from the normal optical methods (for example, the Fabry–Pérot interferometer or other similar apparatus) that the changes in photocurrent are now in the audio frequency range, whereas the frequency changes which define the shape of the spectral line are centred on the optical frequency $\omega_0 \cong 10^{15}$–10^{16} Hz.

The procedure can be illustrated as follows. Let a light wave of amplitude E_0 and frequency ω_0 fall on the scattering particles 1 and 2 in a state of Brownian motion with velocities v_1 and v_2. The light scattered by these particles (observed at an angle θ) will contain the Doppler frequency shifts $\Delta\omega_1$ and $\Delta\omega_2$ with respect to the base frequency ω_0. To simplify the discussion we shall assume equal amplitudes E_1 and E_2 of the components scattered by particles 1 and 2 in the light wave incident on the FEU photocathode. Since the current at the output of the FEU is proportional to the square of the amplitude of the light wave, and the FEU cannot resolve frequencies above 10^9 Hz, we can express the current I by the formula

$$I = \text{const} + E^2 \cos(\Delta\omega_1 - \Delta\omega_2)t .$$

Since $\Delta\omega_1$ and $\Delta\omega_2$ are ~10^3–10^4 Hz it follows from this equation that the photocurrent at the FEU output is modulated by two audio frequencies. In practice, of course, the shifted frequencies of the light wave ($\Delta\omega$) form a complex spectrum which characterises the system and is reflected in the frequency dependence of the photocurrent. Since the beat frequencies of the photocurrent are in the audio region they can be analysed with standard spectral frequency analysers used in radio technology. Their resolving power is usually better than 10 Hz, which is several orders better than the resolving power of ordinary optical spectroscopy equipment.

Two experimental arrangements can be used[9] to extract from the scattered light spectrum the signal carrying information on the kinetic parameters of the scattering macromolecules. In the first (homodyne) assembly the beam of scattered light strikes the surface of the photocathode, where interference between the frequencies contained in the spectral line can take place. In this case the wave whose frequency corresponds to the maximum of the spectral line of the scattered light acts as the reference wave. A beat signal centred on the frequency 0 Hz appears at the output of the FEU. In the second (heterodyne) scheme a reference (base) beam of light of frequency ω_b, obtained from a separate source, is directed at the photocathode together with the experimental beam of scattered light. In this case the beat signal is centred on the frequency $\omega_0 - \omega_b$. If the same laser is used as the base source and for generating the signal, $\omega_0 - \omega_b = 0$, and the signal is centred on the frequency 0 Hz (as in the homodyne variant).

We note that the description "centred" is applied to the beat signal on the understanding that only frequencies $\omega > 0$ have a real significance, i.e. the beat signal has only one branch. We should also stress that so far no really ambiguous names have been proposed for the two variants described above. In particular, the homodyne method has been called the self-beat method[10].

At present the homodyne method of producing beat signals is the more widely used. In the homodyne scheme the photocurrent duplicates the outline of the scattered line (except for a d.c. component and the shot noise of the FEU), but with double the width:

$$I(\omega) = C_1 \frac{2q^2D}{(\Delta\omega)^2 + (2q^2D)^2} , \qquad (10)$$

In the heterodyne scheme the outline of the photocurrent line exactly duplicates that of the scattering line of the spectrum.

A typical homodyne assembly[19] for measuring $\mathcal{I}_{vv}$ at different scattering angles θ is shown in Fig. 1. It consists of a circular photoelectric nephelometer in which the intensity of scattered light can be measured for angles in the range $\theta = 30$–$150°$. The experimental solution is placed in the cylindrical cell K, on which the light of a He–Ne laser ($\lambda_0 = 632.8$ nm) is focussed by the diaphragms D_1 and D_2 and the lens L_1. To optimise the signal-to-noise ratio the scattering volume and its reflection on the photocathode should be as small as possible[9]. By focussing the laser radiation the beam diameter can be reduced to 0.2–0.3 mm. The scattered light is focussed on the photocathode of the FEU by the diaphragm D_3 and L_2, whose focal length is chosen to give an image on the photocathode smaller than the diameter of the light beam in the measuring cell K. The photocurrent from the output of the FEU is taken to the KP amplifier, which has linear frequency characteristics and a stable gain at audio frequencies. The d.c. component of the FEU output is eliminated by a capacitor and the current from the KP is led to the input of the spectrum analyser SA (standard radiotechnical model).

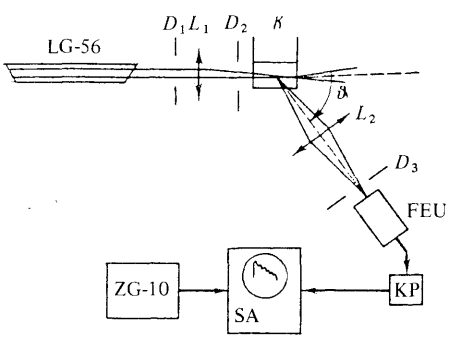


Figure 1. Homodyne variant of the apparatus for studying the dynamic scattering of light in polymer solutions[19]

The spectral distribution of the intensity of scattered light is displayed by analysing the frequency dependence of the photocurrent, $I(\omega)$, at the output of the SA. The photocurrent is characterised by comparing it with the mathematically expected signal and its frequency dependence. The audio frequency generator ZG-10 is used to calibrate the frequency scale of the scan of the SA oscilloscope. The frequency at which the signal is 3 dB down is measured for $\Delta\nu = (\Delta\omega)/2\pi \to 0$. This frequency $(\Delta\nu)_{1/2}$ is assumed to be equal to the half-width of the photocurrent line. In the

homodyne variant the parameter $(\Delta\nu)_{1/2}$ is related to the diffusion coefficient by the equation

$$2\pi(\Delta\nu)_{1/2}=(\Delta\omega)_{1/2}=2q^2D\ , \qquad (11)$$

measured at different values of θ and extrapolated to $\theta = 0$ the intercept on the vertical axis is

$$(\Delta\omega)_{1/2}=6D_r\ , \qquad (12)$$

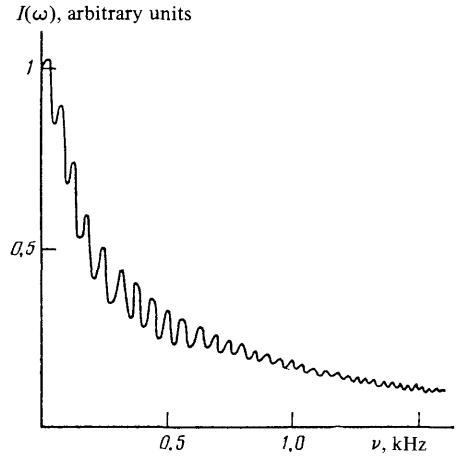


Figure 2. Outline of the photocurrent line on the screen of the spectrum analyser for a solution of the $M = 10^7$ fraction of polystyrene in toluene; $c = 0.05\%$, scattering angle $\theta = 60°$.[19]

A typical plot of the photocurrent against frequency at the FEU output, photographed from the screen of the spectrum analyser, is shown in Fig.2.

IV. SOME EXPERIMENTAL RESULTS

Measurements of $(\Delta\omega)_{1/2}$ as a function of θ are shown in Fig.3 for some polymer solutions. The D values calculated from the slope of the lines are given in Table 1 together with the D values obtained by an independent method (polarisation interferometry). The concentration of the solutions were the same in both sets of measurements (~0.05%). As Table 1 shows, the agreement between the D values obtained by the two methods is acceptable.

We note that the extrapolation of curve *2* in Fig.3 does not pass through the origin. This effect is due to the anisotropic component of the light scattered by polystyrene (PS) solutions. It follows that at the highest molecular weights the amplitude modulation of the light scattered by PS solutions is large enough to be experimentally detectable. Amplitude modulation of the scattered light results from the rotational motion of macromolecules showing optical anisotropy.

The $\mathcal{J}_{VV}$ spectrum of the scattered light for an anisotropic molecule is the sum of at least two Lorentzian curves according to Eqn.(8). The half-width is determined by the parameters D and D_r, and the contribution from the translational diffusion decreases as the scattering angle decreases. In principle this allows us to separate the component due to molecular rotation from the overall spectrum. If $(\Delta\omega)_{1/2}$ is

Table 1. Diffusion coefficients D for some polymers, determined by dynamic light scattering and by measurements of longitudinal diffusion in solutions[19].

Polymer	Solvent	$10^{-6}M$	$10^{11}D$, $m^2 s^{-1}$	
			light scattering	longitudinal diffusion
Polystyrene	toluene	1.0	1.3	1.4
Polystyrene	»	13.0	0.6	0.5
Styrene–methyl methacrylate block copolymer	butyl acetate	0.6	1.6	1.8
Polyvinyltrimethylsilane	cyclohexane	0.5	1.0	1.04

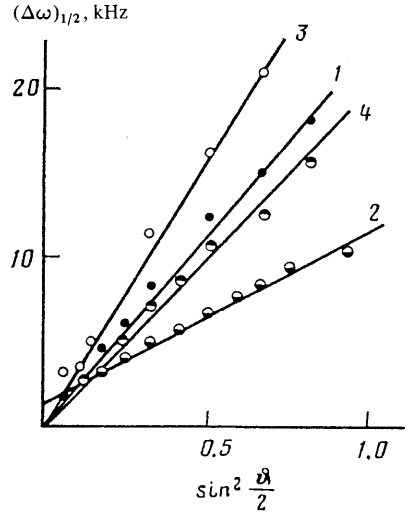


Figure 3. Plots of the half-width of the scattering angle $(\Delta\omega)_{1/2}$ against $\sin^2\theta/2$ for polystyrene (*1*, *2*), the styrene–methyl methacrylate block copolymer (*3*), and polyvinyltrimethylsilane (*4*).[19]

Experiments of this type for F-actin are reported in Ref. 20. The D_r values calculated by Eqn.(12) were close to the values given by other methods for this polymer.

An analysis of the frequency dependence of $\mathcal{J}_{VV}$ has been reported[21] for the PS fraction with $M = 10^7$ in benzene and decalin. An appropriately oriented Frank–Ritter prism was inserted into the scattered light path of the apparatus shown in Fig.1 to separate $\mathcal{J}_{VV}$ from the overall scattered intensity. The root mean square radius of inertia of the PS molecule in benzene was found to be $(\overline{R^2})^{1/2} = 140$ nm from the light scattering results. This value of $(\overline{R^2})^{1/2}$ accounted for a change from 6 to 1 in $x = q^2\overline{h^2}/6 = q^2\overline{R^2}$ for solutions in benzene over the working range of scattering angles. The range of x values for solutions of PS in decalin was calculated from the radius of inertia of the PS macromolecules

obtained by Flory's formula from the characteristic viscosity. The choice of these solvents was dictated by the difference in their thermodynamic properties in relation to PS and by the large difference in their viscosities.

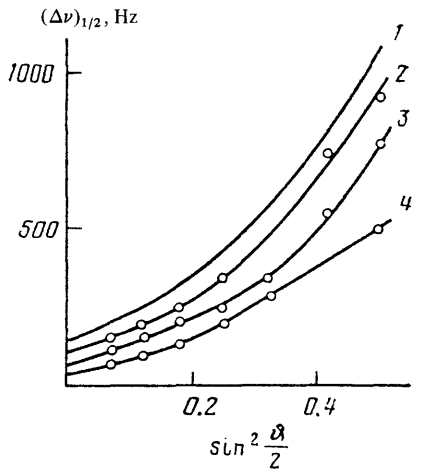


Figure 4. Plots of the half-width of the scattering line $(\Delta\nu)_{1/2}$ against $\sin^2\theta/2$ for solutions of the $M = 10^7$ fraction of polystyrene in toluene at different concentrations: *1*) 0; *2*) 0.06; *3*) 0.12; *4*) 0.18 g/100 cm^3.[21]

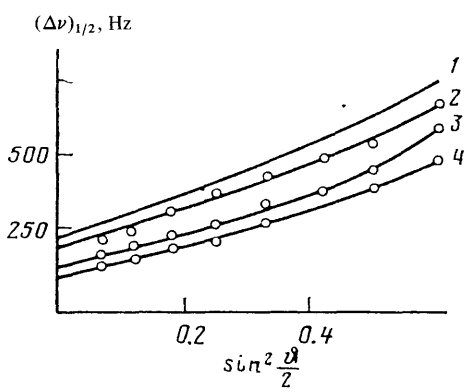


Figure 5. Plots of the half-width of the scattering line $(\Delta\nu)_{1/2}$ against $\sin^2\theta/2$ for a solution of the $M = 10^7$ fraction of polystyrene in decalin at different concentrations: *1*) 0, *2*) 0.05, *3*) 0.12, *4*) 0.17 g/100 cm^3.[21]

The dependence of $(\Delta\nu)_{1/2}$ on $\sin^2\theta/2$ for solutions of PS in benzene and in decalin at different concentrations is shown in Figs.4 and 5. The shape of the scattering line at all the concentrations can be described as the sum of at least two Lorentz curves, as indicated by the non-linearity of the plots in Figs.4 and 5. The width of the spectral distribution of the scattered light intensity increases as the concentration of the solution decreases. The results were therefore extrapolated to zero concentration. Fig.6 shows the dependence of $(\Delta\nu)_{1/2}$ on the concentration of the solution c for the scattering angle $\theta = 0$: the plot is linear within experimental error. Linear plots of $(\Delta\nu)_{1/2}$ against c were obtained also for other (non-zero) scattering angles. Plots of $(\Delta\nu)_{1/2}$ against $\sin^2\theta/2$ for $c = 0$ are shown as the upper lines in Figs.4 and 5. Extrapolation of the data in Fig.6 to $\theta = 0$ gave the $(\Delta\nu)^0_{1/2}$ values: the half-widths of the scattering spectra for $\theta = 0$ and $c = 0$. The $(\Delta\nu)^0_{1/2}$ values were used to calculate the rotational diffusion coefficients of the PS molecules in benzene and decalin by the equation

$$2\pi(\Delta\nu)^0_{1/2} = (\Delta\omega)^0_{1/2} = 2 \cdot 6D_r \,. \qquad (13)$$

The D_r values and some physical parameters of the PS solutions are given in Table 2.

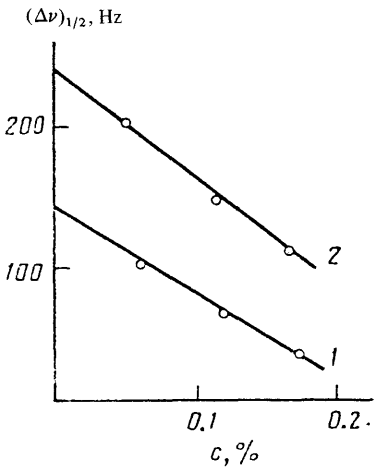


Figure 6. Dependence of $(\Delta\nu)_{1/2}$ at the scattering angle $\theta = 0$ on the concentration of the solution (c) for the $M = 10^7$ fraction of polystyrene in toluene (*1*) and in decalin (*2*).[21]

Table 2. Physical characteristics of solvents and of the solutions of the $M = 10^7$ fraction of polystyrene[21]

Solvent	$10^3\eta_0$, Pa s	x	D_r, s^{-1}	
			light scattering	FBR
Benzene	0.64	1—6	120	100
Decalin	2.07	0.6—3.4	80	—

At low values of the scattering angle θ the parameter $\mathcal{J}_{vv}$ is controlled by the first term of Eqn.(8). Under these conditions the dependence of $(\Delta\nu)_{1/2}$ on $\sin^2\theta/2$ is described by a straight line whose slope is proportional to the translational diffusion coefficient D. Using the homodyne method of detecting the scattered light we find, for small θ,

$$2\pi[(\Delta\nu)_{1/2} - (\Delta\nu)^2_{1/2}] = 2q^2D \,. \qquad (14)$$

The diffusion coefficients of the PS fraction calculated for $c = 0$ from the initial slope of the curves in Figs.4 and 5 are $D = 0.4 \times 10^{-11}$ m^2 s^{-1} in benzene and 0.2×10^{-11} m^2 s^{-1} in decalin.

It is interesting to compare the D_r values obtained in this way with data on the rotational diffusion coefficient of PS in benzene calculated from measurements[22] of flow birefringence (FBR). According to those measurements, $D_r = 100$ s^{-1} for the $M = 10^7$ fraction of PS. This is acceptably close to the value $D_r = 120$ s^{-1} given by the dynamic light scattering method (see Table 2). The difference between the two values is probably due partly to the difference between the methods of determining D_r and partly to the dependence of $\mathcal{I}_{VV}$ on the mode of dispersion of the sample. The effective spectral broadening (and therefore also the D_r value) for $x < 10$ is greater for polydispersed than for monodispersed samples[23].

The role of the second term in Eqn.(8), which according to Eqn.(9) is proportional to $(\alpha_\parallel - \alpha_\perp)^2$, increases markedly with the anisotropy of the macromolecules. In principle, the anisotropic component $\mathcal{I}_{HV}$ can be measured at the scattering angle $\theta = 0$. This allows complete elimination of the Doppler effects due to the translational motion of the macromolecules on the spectral distribution[24,25]. From Eqn. (9) for $\theta = 0$ we obtain

$$\mathcal{I}_{Hv} = \frac{NA}{9\pi}(\alpha_\parallel - \alpha_\perp)^2 \frac{6D_r}{(\Delta\omega)^2 + (6D_r)^2} .$$

Under these conditions the scattering spectrum has a simple Lorentz outline. The half-width of the spectrum is determined by Eqn.(12). Hence there are at least two possible ways of decoupling the component contributed by the rotation of an anisotropic molecule from the scattering spectrum: extrapolation of the data obtained from measurements of $\mathcal{I}_{VV}$ to zero angle of scattering and direct measurements of $\mathcal{I}_{HV}$ at $\theta = 0$.

Parallel measurements of the angular dependence of $\mathcal{I}_{VV}$ and of the parameter $\mathcal{I}_{HV}$ at $\theta = 0$ have been made on solutions of three samples of poly-γ-benzyl-*L*-glutamate (PBG) in dimethylformamide (DMFA).[21] Because of their rigidity the molecules of this polymer have a high segmental anisotropy: $(\alpha_\parallel - \alpha_\perp) = 400 \times 10^{-23}$.[26] This is almost two orders of magnitude higher than typical values for polymers with flexible chains. Hence in the case of solutions of PBG in DMFA we can extract the anisotropic component from the overall spectrum with confidence.

The parameter $\mathcal{I}_{VV}$ for solutions of PBG in DMFA was measured at different angles of scattering by the apparatus shown in Fig.1. On the other hand, for measurements of $\mathcal{I}_{HV}$ at $\theta = 0$ the following optical assembly was used. The experimental solution was placed in a glass cell in the shape of a tube 15 mm in diameter and 10 cm long in the path of the light beam. The cell was located between crossed Frank–Ritter prisms, one of which (at the point of entry of the beam into the cell) polarised the laser light in a vertical plane, while the other (following the cell) separated the $\mathcal{I}_{HV}$ component of the scattered light. Because the polarisation by the prisms was not perfect, part of the primary beam reached the photocathode of the FEU. The horizontal component of this primary beam, which had an elliptical polarisation, was used as the reference beam in the heterodyne detection method. The current from the FEU was taken to a specially designed amplifier, assembled from micro-modules, incorporating high- and low-frequency corrections and having a high gain at audio frequencies. The signal was then passed to the input of the spectrum analyser. The spectral distribution of the photocurrent observed on the SA screen had the same width as the scattering spectrum[9]. All the recorded spectrograms were similar to those shown in Fig.5.

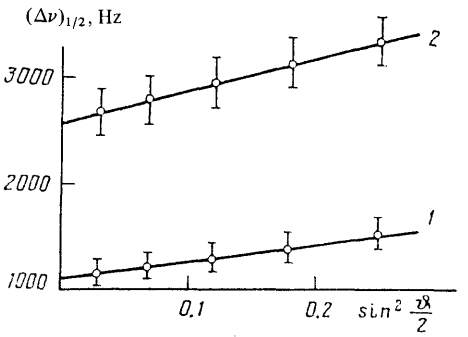


Figure 7. Dependence of $(\Delta\nu)_{1/2}$ on $\sin^2\theta/2$ for solutions of PBG samples 1 and 2 in DMFA.[21]

Table 3. Experimental data for solutions of PBG in DMFA.[21]

Sample	$10[\eta]$, m^3 kg^{-1}	$10^{13}s$, s	$10^{-3}M_\eta$	$10^{-3}M_{s\eta}$	$10^{11}D$, m^2 s^{-1}	$10^{-3}M_{sD}$	D_r, s^{-1} from $\mathcal{I}_{Hv}$	D_r, s^{-1} from $\mathcal{I}_{vv}$	D_r, s^{-1} from FBR
1	8.2	3.5	370	330	0.84	360	630	570	580
2	3.7	3.0	220	180	1.30	220	1160	1400	1350
3	0.8	2.2	83	70	—	—	5900	—	6600

Symbols: $[\eta]$ is the characteristic viscosity; s is the sedimentation coefficient; M_η is the molecular weight of PBG calculated from the $[\eta]$ value by the Mark–Koene equation; $M_{s\eta}$ is the molecular weight calculated from $[\eta]$ and s using the hydrodynamic constant A_0; M_{sD} is the molecular weight calculated from sedimentation and diffusion data.

Fig.7 shows the dependence of $(\Delta\nu)_{1/2}$ on $\sin^2\theta/2$ for PBG samples 1 and 2, plotted from measurements of the angular dependence of the $\mathcal{I}_{VV}$ spectrum. We note that the plots do not go through the origin. A corresponding plot for sample 3 could not be obtained because of the high noise level and the large width of the spectrum. The curves in Fig.7 were used to calculate the translational diffusion coefficients D of samples 1 and 2 by formulae (14). The results are given in Table 3 with the molecular weights of the PBG samples. The M values were determined in various ways: from characteristic viscosity $[\eta]$ data, inserted into the equations of Mark and Koene[26], from sedimentation and viscosimetric data, using the hydrodynamic constant $A_0 = 4.1 \times 10^{-17}$ J K^{-1}, and in the case of samples 1 and 2 from measurements of D and s, where s is the sedimentation coefficient[26]. The similarity between the M values obtained by different methods suggests that the PBG samples are not significantly polydispersed.

The rotational diffusion coefficient D_r is calculated from the intercept on the vertical axis of the plot of $(\Delta\nu)_{1/2}$ against $\sin^2\theta/2$ (Fig.7). In the homodyne variant of the detection system the quantities $(\Delta\nu)^0_{1/2}$ and D_r are related by Eqn.(13). It follows from Fig.7 that for the PBG samples

1 and 2 the $(\Delta\nu)^0_{1/2}$ values are (respectively) 1100 ± 100 and 2600 ± 200 Hz. The D_r values derived from these[21] by formula (13) are given in Table 3.

The second method of determining D_r consists in finding $(\Delta\nu)_{1/2}$ for the scattering angle $\theta = 0$ for the $\mathcal{J}_{H\nu}$ spectrum[24]. In the heterodyne detection variant the quantity $(\Delta\nu)_{1/2}$ is related to the rotational diffusion coefficient by the expression

$$2\pi(\Delta\nu)_{1/2} = (\Delta\omega)_{1/2} = 6D_r \ . \qquad (15)$$

The values of $(\Delta\nu)_{1/2}$ determined from the photocurrent spectra for the PBG samples 1, 2, and 3 were 600 ± 50, 1100 ± 100, and 5600 ± 500 Hz respectively at $\theta = 0$. These values were used to calculate the rotational diffusion coefficients D_r (also given in Table 3).[21] It is evident that the two methods of calculating D_r give similar results.

These values can be compared also with measurements[26] of the rotational diffusion coefficient of PBG in DMFA by the dynamic flow birefringence method. Values of D_r calculated from those measurements for PBG fractions of molecular weight corresponding to samples 1, 2, and 3 are also given in Table 3. We note that the D_r values calculated from the dynamic flow birefringence are close to those obtained by the dynamic light scattering method.

The measurement of D by the dynamic light scattering method has some important advantages over the conventional refractometric methods. Firstly, the principle of the measurement is more rational: we observe "self-diffusion" rather than diffusion across a boundary. Thus the creation of a solvent–solution diffusion boundary becomes unnecessary. The measurements of D are carried out under conditions of strict thermodynamic equilibrium. The measurement time is much shorter: a measurement of the angular dependence of $\mathcal{J}_{\nu\nu}$ and calculation of D can be completed in 15–20 min, whereas a refractometric determination of D usually requires at least 24 h. Because of the shorter experimental times the requirements on the temperature stability of the experimental cell are less demanding. On the other hand, like all light scattering experiments, the method requires painstaking purification of the solutions and cleaning of the cells[3].

V. FURTHER DEVELOPMENTS OF THE METHOD

The dynamic light scattering method has been used not only to determine the hydrodynamic characteristics of macromolecules (D,[27,28] D_r,[29] and the parameters of the intramolecular motion and of the relaxation processes in polymer chains[30,31]), but also to study cooperative diffusion in concentrated polymer solutions[32] and chain mobility in polymer gels[33], and to monitor the dynamics of the formation of critical fluctuations in polymer solutions[34] and molecular motion in polymer networks[16] and in polymer films adsorbed on a different polymer[35]. Attempts have been made to apply the dynamic light scattering method in studies of the kinetics of chemical reactions[8,17,18,36].

Dynamic light scattering assemblies incorporating minicomputers (correlometers) for direct calculation of the correlation function $G_\phi(\tau)$ are now widely used[9,37]. In the homodyne method of recording the photocurrent the autocorrelation function $G_\phi(\tau)$ is simply related to the autocorrelation function of the photocurrent $G_I(\tau)$ by the expression[37]

$$G_I(\tau) \approx 1 + f|G_\varphi(\tau)|^2 \ , \qquad (16)$$

where the constant $f \leq 1$ is a correction for incoherent effects and for the finite time of flight of electrons. Inserting the expression (3′) for $G_\phi(\tau)$ into Eqn.(16) gives

$$G_I(\tau) = 1 + f\exp(-2q^2D\tau) \ . \qquad (17)$$

This equation applies to small isotropic particles for $x < 1$. In the case of anisotropic molecules the spectrum of the scattered light ($\mathcal{J}_{\nu\nu}$) is given by Eqn.(8). The autocorrelation function of the photocurrent $G_I(\tau)$ in this case becomes, to a first approximation,

$$G_I(\tau) = 1 + C_1\exp(-2q^2D\tau) + C_2\exp[-(q^2D + 6D_r)\tau] \ , \qquad (18)$$

where C_1 and C_2 are constants. We note from formulae (17) and (18) that the autocorrelation function of the photocurrent is a simple exponential or the sum of two exponentials. This greatly simplifies the interpretation of the results and the calculation of D and D_r.

The most noteworthy of the assemblies developed for analysing the spectral distribution of the light it is the quadratic detection spectrometer described in Ref.38. It can be used to analyse the spectral distribution of light intensity in scattered light. A special attachment to this spectrometer for calculating the autocorrelation function $G_\phi(\tau)$ has also been developed[39].

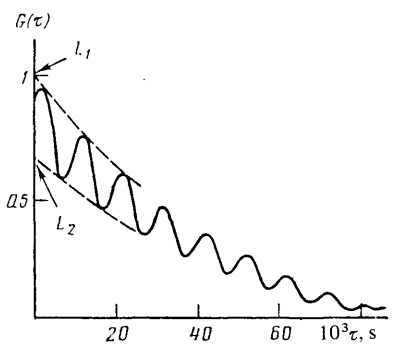


Figure 8. Autocorrelation function for the light scattered by a polystyrene suspension in a vibrating cell[40].

We should note a further potential application of dynamic light scattering. Japanese workers[40] have proposed a new method of determining the sedimentation coefficient of dissolved particles. Vibrational acceleration is applied to the polymer solution by setting the cell and the solution in vibrational motion with a frequency ω_V and amplitude a_V. The autocorrelation function of the photocurrent in this case is an exponential [given, for example, by Eqn.(17) with a superimposed sinusoidal oscillation of frequency ω_V produced by the sedimentation motion of the particles (Fig.8)]. The amplitude of these oscillations is proportional to the amplitudes a_i of the relative displacement of the particles in the solution. On the spectral distribution of the photocurrent this autocorrelation function corresponds to two maxima with a Lorentz outline and centred on the frequencies $\omega = 0$ and $\omega = \omega_V$. The parameter a_i can be evaluated from the ratio of the heights of these maxima. The average sedimentation coefficient is given by the expression

$$(\overline{s^2})^{1/2} = \frac{1}{a_V\omega_V}\left(\sum A_i a_i^2\right)^{1/2} \ , \qquad (19)$$

where A_i is the relative intensity of the light scattered by the *i*th particle. Formula (19) applies to the heterodyne variant of the method of light detection. The degree of polydispersion of the dissolved particles can also be obtained if the homodyne variant of the apparatus is used.

By solving the equation of motion for the *i*th particle of a solution in a vibrating cell in terms of the autocorrelation function $G_I(\tau)$ and averaging over all the particles the authors[40] converted Eqn.(19) into

$$s = \frac{1}{a_v \omega_v} \frac{L_1 - L_2}{L_1} \quad (20)$$

where L_1 and L_2 are the intercepts obtained by extrapolating to the ordinate axis the envelopes of the sinusoidal modulation of the autocorrelation function $G_I(\tau)$ shown in Fig.8. Formula (20) is valid for small vibration amplitudes a_v, and it offers a practical method of calculating *s* from dynamic light scattering data. The criterion for smallness of the vibration amplitude of the cell is a displacement a_i during one vibration period smaller than the wave length of the laser radiation.

As well as *s* we can determine the translational diffusion coefficient *D* from the upper envelope of the autocorrelation function $G_I(\tau)$, using (for example) Eqn.(17). Of course, this parameter can also be determined by studying light scattering without vibration of the cell.

The original paper[40] describes a study of the sedimentation of a suspension of polystyrene latex in water by this method. The sedimentation coefficient of the latex measured in an ultracentrifuge was $s = 2.81 \times 10^{-7}$ s, and the value calculated by Eqn.(20) from the autocorrelation function of the scattered light was 3.0×10^{-7} s. Thus the effectiveness of the proposed method of determining *s* from measurements of dynamic light scattering was convincingly demonstrated. There is no evidence that the method has been adopted in other laboratories so far, but any attempt to develop new methods of determining sedimentation coefficients without resorting to the traditional ultracentrifuge techniques cannot fail to attract interest.

To conclude this review we should mention one more method, developed during the past 2 or 3 years: the use of holography in studies of dynamic light scattering[41]. The holographic correlometer with phase modulation has been used successfully in studies of ultra-slow molecular motions in very viscous scattering media[41].

The dynamic light scattering method offers some important advantages over the traditional methods of studying the translational and rotational mobility of macromolecules. These advantages are discussed above. However, the apparatus which has to be used to analyse the frequency dependence of the photocurrent is fairly complex. The experimenter must have had some previous experience of working with a spectrum analyser, and he must be familiar with modern methods of correlation analysis, including the use of correlometers (a highly specialised form of digital computer).

New fields of application of dynamic light scattering have been identified in recent years. In addition to the existing studies of the mobility of polymeric molecules[42], the properties of polyelectrolyte solutions at different ionic strengths have been investigated[43,44]. Dynamic light scattering is being studied in concentrated solutions and in gels[45], and the transition temperature in macromolecular systems (polystyrene[46] and poly(methyl methacrylate)[47]) are being determined. Additions to this list in the near future are likely. Thus we may conclude that the dynamic light scattering method is being successfully developed.

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"50th Anniversary of the USSR"
Syktyvkar State University

Russian Chemical Reviews

June 1984

Translated from *Uspekhi Khimii*, 53, 897-924 (1984)

U.D.C. 547.245 + 539.194

The Photoelectron Spectra and Molecular-orbital Characteristics of Covalent Aromatic Organoelemental Compounds

V.F.Traven' and B.I.Stepanov

The effects of the interaction of various heteroatoms (and heteroatomic fragments) with carbon π-electron systems in covalent organoelemental compounds are discussed in the review in terms of molecular orbital theory. Particular attention is devoted to the analysis of the structure of the molecular orbitals, determined from photoelectron spectroscopic data and quantum-chemical calculations within the framework of the simple Hückel molecular orbital method parametrised on their basis. It is shown that the parameters characterising the mixing of the orbitals in model compounds can be used to obtain the molecular-orbital characteristics and to interpret the spectroscopic properties and reactivities of complex heteroaromatic compounds.
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I. INTRODUCTION

The photoelectron spectra of aromatic organoelemental compounds, in which the heteroatoms are present in substituents or rings, together with the corresponding quantum-chemical calculations within the frameworth of the simple method make it possible to estimate the orbital mixing parameters of individual fragments in the molecules of these compounds and to obtain objective data for the molecular orbitals (MO), which determine the spectroscopic properties and reactivities of the compounds. Such information is important for the study of problems of chemical bonding within the framework of the molecular orbital theory and for the solution of practical problems—the establishment of new aromatic organoelemental systems[1], the synthesis of effective π-donors[2-5], the synthesis of phototropic compounds[6,7], etc. The interaction of the orbitals in aromatic organoelemental compounds has been analysed in reviews[8-11] concerned with the study of the influence of various substituents on the ionisation energies of substituted benzenes; the role of unoccupied *d* orbitals in certain organoelemental compounds has been discussed[12-16] and the ability of the atoms of heavy elements to form double bonds with carbon and with one another, etc. has been considered[17,18].

This review presents a survey of the quantitative estimates for the mixing of the orbitals of the π-electron systems of the carbon atoms and various non-carbon element-containing substituents and fragments incorporated in the rings. The estimates have been obtained from the analysis of the photoelectron spectra (PES) of the corresponding compounds and from quantum-chemical calculations within the framework of the simple method. We shall consider some aspects in greater detail.

In both non-empirical and semiempirical quantum-chemical calculations the orbitals of whole groups or molecular fragments rather than the atomic orbitals (AO) are used as the basis orbitals. In non-empirical calculations this is the SAMO method (simulated *ab initio* technique)[19,20], while in semiempirical calculations it is the group orbital method[20-24], which explains successfully the spectroscopic properties of many organic and organoelemental compounds[25-27]. Following the development of PES, the corresponding computational schemes have been applied effectively also in the simple quantum-chemical approximations[28,29]. Within the framework of such calculations, the molecular orbital is treated as a linear combination of bond orbitals in the LCBO-MO method[30-32], for example, while in the LCFO-MO scheme[33] it is treated as a linear combination of fragment orbitals. Despite the differences between the names and in certain specific problems, the essential features of the above schemes are identical; instead of atomic orbitals, "effective" orbitals, for example those of the individual molecular fragments, are considered in the basis set. Such schemes make calculations significantly less laborious and yield a particularly large amount of information in the study of the electronic and molecular structures of complex organoelemental compounds and in the first place compounds containing the elements of high Periods for which there are frequently no parameters in semiempirical methods.

In the solution of the Roothaan equations

$$\sum_{\mu=1}^{N} c_{\mu i}\,(H_{\mu\nu} - \varepsilon_i \delta_{\mu\nu}) = 0\,,$$

where μ and ν are the indices of the basis fragment orbitals, i is the index of the molecular orbital, $c_{\mu i}$ and ε_i are the coefficients and energies of the molecular orbitals, and $\delta_{\mu\nu} = 1$ (for $\mu = \nu$) or 0 (for $\mu \neq \nu$) is the Kronecker delta, by the simple method (Hückel's π-approximation), the influence of the interelectron interaction is taken into account implicitly in the parametrisation of the skeletal integrals $H_{\mu\mu}$ and $H_{\mu\nu}$. In particular, compared with the rigorous semiempirical methods in which the skeletal integrals are parametrised on the basis of atomic spectroscopic data, in the simple method the parametrisation based on molecular electronic spectra is apparently more useful: it has been suggested that $H_{\mu\mu}$ and $H_{\mu\nu}$ be estimated from photoelectron spectroscopic data for "model" compounds in which the corresponding μth and νth orbitals of the fragments are characterised by unoverlapped ionisation bands[28-31]. The parameters $H_{\mu\mu}$ and $H_{\mu\nu}$ found from the molecular spectra include to some extent the interelectronic effects (see below).

In terms of the π-approximation, only those fragment orbitals which have π-symmetry (or are close to it) relative to the molecular plane are included in the basis set of the simple calculation. For example, within the framework of the method of fragment orbitals, the integral H_S, corresponding to the $3p_\pi$ orbital of the sulphur atom in heterocyclic and heteroaromatic compounds, is estimated from the PES of compounds in which the sulphur atom is linked to two carbon atoms, in particular, the spectra of dimethyl sulphide[35] and not from the atomic spectrum of sulphur (where the ionisation potential of the $3p$ orbital is 13.32 eV[34]) and not from the PES of hydrogen sulphide (the ionisation potential of the b_1 orbital formed by the $3p_\pi$ orbital of sulphur is 10.47 eV[30]). One should bear in mind that in a compound of this kind (C_{2v} symmetry group) not only the $3p_\pi$(S) atomic orbital but also the (+)-combination of the $2p_\pi$ orbitals of two carbon atoms belong to type b_1. For this reason, the highest occupied molecular orbital ($2b_1$ orbital) of dimethyl sulphide is not identical with the p orbital of the sulphur atom, although it is generated predominantly by this orbital†:

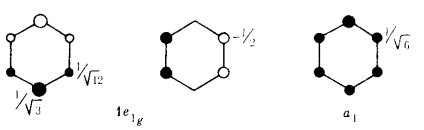
$$H_S = -I_{2b_1}^{SMe_2} = -8.67 \text{ eV}\,.$$

It is important to note that a further increase in the complexity of the molecule of the "model" compound alters little the parameter $H_{\mu\mu}$. For example, $H_S = -8.80$ eV, estimated in terms of the ionisation potential of the $3p_\pi$ orbitals of two sulphur atoms from the PES of 1,4-di(methylthio)benzene[30], differs only slightly from $H_S = -8.67$ eV found from the PES of dimethyl sulphide.

The parameters corresponding to the fragment orbitals localised predominantly at the atoms of other Group V–VII elements can be found analogously by simple quantum-chemical calculations in terms of the π-approximation; in this review these parameters are denoted respectively by H_O, H_{Se}, H_N, H_{Br}, etc.

The fragment orbitals involving the sp^3-hybridised orbitals of the atoms of Group IVA elements are taken into account in the calculations under consideration within the framework of the $\sigma-\pi$ conjugation scheme. The possibility of the overlap of the orbitals of the π- and σ-bonds located in a single plane but directed at an angle ϕ relative to one another has been discussed in detail in connection with the hyperconjugation model[36] and in another study[37] where this model was developed for organoelemental benzene derivatives. The integrals $H_{\mu\mu}$ corresponding to the σ(E–S) orbitals, are estimated from the first ionisation potentials of the compounds EMe_4: the orbitals of the four σ(E–C) bonds of the tetrahedral EC_4 fragment transform within the framework of the T_d symmetry group as $3t_2 + 1a_1$ and the triply degenerate t_2 orbital proves to be the highest occupied orbital. The corresponding diagonal matrix elements $H_{\mu\mu}$ will henceforth be designated by H_{EC}.

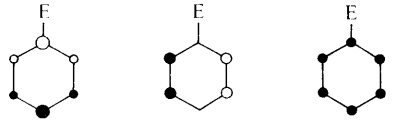
For the purpose of the present review, the π orbitals of aromatic hydrocarbons which can mix with the orbitals of the heteroatoms in heteroaromatic compounds are of special interest. The molecular orbitals of benzene have been studied in many investigations[38-45]. For example, according to the data of Dewar et al.[43] three π orbitals of benzene (the classification corresponds to the D_{6h} symmetry group) belong to types e_{1g} and a_{2u} and have the following coefficients (the filled circles correspond to positive coefficients and the open circles to negative coefficients; the size of the circles is proportional to the absolute magnitude of the coefficient):



It is known from the PES of benzene that the ionisation potential of the a_{2u} orbital is 12.23 eV[43] and the two degenerate e_{1g} orbitals have identical energies (their ionisation potential is 9.24 eV). Their degeneracy is removed after the introduction of a substituent E into the benzene molecule. In monosubstituted benzene derivatives C_6H_5E (C_{2v} symmetry) the benzene π orbitals transform as b_1, a_2, and b_1:

† According to a calculation by the extended Hückel method, the contribution of the $3p_\pi$ orbital of the sulphur atom is not less than 85% of the highest occupied molecular orbital (HOMO) of dimethyl sulphide.

they have come to be designated as the $\varphi_{\pi(sym)}$, $\varphi_{\pi(asym)}$, and φ_{π_1} orbitals respectively#:



$\varphi_{\pi(sym)}$, b_1 $\varphi_{\pi(asym)}$, a_2 φ_{π_1}, b_1

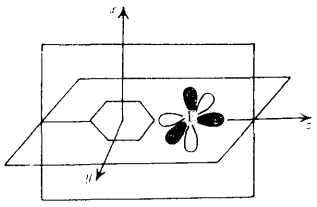
In conformity with the foregoing, in quantum-chemical calculations parametrised on the basis of PES data (simple method, π-approximation), the following diagonal elements $H_{\mu\mu}$ have been adopted for the benzene π orbitals as the fragment integrals:

$$H_{\pi(sym)} = H_{\pi(asym)} = -9.24 \text{ eV}; \; H_{\pi_1} = -12.23 \text{ eV}.$$

"Model" compounds in the PES of which an ionisation band corresponding to a linear combination of the μth and νth fragment orbitals is observed are used to estimate the non-diagonal integrals $H_{\mu\nu}$. By determining the corresponding ionisation potential I_i from the PES and setting $I_i = -\varepsilon_i$, one can find the parameter $H_{\mu\nu}$ from the secular equation

$$\begin{vmatrix} (H_\mu - \varepsilon_i) & H_{\mu\nu} \\ H_{\mu\nu} & (H_\nu - \varepsilon_i) \end{vmatrix} = 0 \; . \qquad (1)$$

The possibility of the involvement of particular fragment orbitals in the molecular orbitals is determined by their symmetry. For example, benzene derivatives PhE in which the substituents E contain the atoms of Group IV–VII elements (for example, $SiMe_3$, PMe_2, SMe, or Cl) have approximately C_{2v} symmetry. Under the influence of the symmetry operations, three π orbitals of the benzene ring and the p orbitals of the atom E transform as shown below:



C_{2v}	E	C_2^z	$\sigma_v^{(xz)}$	$\sigma_v^{(yz)}$	
φ_{π_1}	+1	−1	+1	−1	b_1
$\varphi_{\pi(sym)}$	+1	−1	+1	−1	b_1
$\varphi_{\pi(asym)}$	−1	+1	−1	−1	a_2
φ_{p_z}(E)	+1	+1	+1	+1	a_1
φ_{p_y}(E)	+1	−1	−1	+1	b_2
φ_{p_x}(E)	+1	−1	+1	−1	b_1

We shall assume that the HOMO of the compound PhE are produced as a result of the mixing of only the $\varphi_{\pi(sym)}$ orbital of benzene and the φ_{p_x} orbital of the heteroatom E. The parameter $H_{E\pi(sym)}$ characterising the degree of mixing of the above fragment orbitals, can then be found from Eqn.(1).

On the other hand, if account is taken of the fact that the HOMO of the substituted benzene is produced as a result of the mixing of not only the φ_{p_π}(E) and the $\varphi_{\pi(sym)}$ orbitals but also the φ_{π_1} orbitals (all these orbitals belong to the same irreducible representation b_1 of the C_{2v} group), then the parameter $H_{E\pi(sym)}$ must be found from the solution of the third-order secular equation

$$\begin{vmatrix} (H_{\pi(sym)} - \varepsilon) & H_{E\pi(sym)} & 0 \\ H_{E\pi(sym)} & (H_E - \varepsilon) & H_{E\pi_1} \\ 0 & H_{E\pi_1} & (H_{\pi_1} - \varepsilon) \end{vmatrix} = 0 \; . \qquad (2)$$

The relations between the non-diagonal elements $H_{\mu\nu}$, characterising the interactions of the benzene π orbitals and the p_π orbital of the heteroatom E, are then employed:

$$H_{E\pi(sym)} \times \sqrt{3} = H_{E\pi(asym)} \times 2 = H_{E\pi_1} \times \sqrt{6} = H_{EC}. \qquad (3)$$

These are selected in accordance with the coefficients of the benzene π orbitals indicated above.

The inclusion of the φ_{π_1} orbital in the basis set alters only slightly $H_{E\pi(sym)}$. For example, the values of $H_{S\pi(sym)}$, obtained by the two methods described above and characterising the mixing of the fragment π orbital localised mainly at the sulphur atom with the benzene $\varphi_{\pi(sym)}$ orbital, are virtually identical: 0.84 ± 0.04 eV and 0.78 ± 0.06 eV respectively.

It must be specially emphasised that Eqn.(3) makes it possible to estimate the parameter H_{EC}, which characterises directly the interaction of the p_π orbital of the heteroatom E with the $2p_\pi$ orbital of the carbon atom.

The effects of the interelectronic interactions are taken into account in the values of the ionisation potentials found from the PES of "model" compounds and hence in the corresponding parameters $H_{\mu\mu}$ and $H_{\mu\nu}$. The quantum-chemical calculations based on this parametrisation procedure can therefore be carried out in terms of the scheme of the simple method without adjustment for self consistency.

Furthermore, the parameters $H_{\mu\mu}$ and $H_{\mu\nu}$, estimated from the ionisation potential obtained from the PES, include the reorganisation energy and the changes in the correlation and relativistic energies accompanying photoionisation. Thus the parametrisation of the quantum-chemical models, based on the PES data, removes to a large extent the limitations of the Koopmans theorem, which are evident in a comparison of the ionisation potentials I_i determined from the PES with the eigenenergies ε_i^{SCF} calculated in terms of the one-electron approximation[46,47]: $I_i = -\varepsilon_i^{SCF}$. This is probably why the quantum-chemical calculations employing the above parametrisation procedure are fairly reliable for the estimation of the electronic and molecular structures of complex organic and organoelemental compounds and are frequently comparable, as regards the amount of information they provide, with the results of much more cumbersome calculations by the self-consistent field (SCF) method.

In the subsequent Sections of this review, PES data for aromatic hydrocarbons and the corresponding aromatic organoelemental compounds will be discussed. The ionisation potentials of the compounds which it is proposed to regard as "model" compounds are compiled in Tables 1–3 and 6. It is noteworthy that the PES of organic compounds of certain elements have been discussed in a number of reviews[48–50]. However, the use of different quantum-chemical models by different investigators for the purpose of interpretation precludes the comparison on the basis of the data in the above reviews of the capacities of the orbitals of different elements for mixing with the π orbitals of carbon atoms. In order to discover the trends in the variation of the molecular-orbital parameters of the corresponding compounds as a function of the atomic number of the element, we present in the same Tables the results of our quantum-chemical analysis of the molecular orbital structures on the basis of the scheme proposed above. The integrals $H_{E\pi}$ and H_{EC} are compared as parameters in terms of which the degree of mixing of the orbitals is to be estimated.

This designation of the orbitals enumerated has been generally adopted for unsubstituted benzene and also in the analysis of the molecular-orbital structures of polysubstituted benzene derivatives and polycyclic compounds involving heteroatoms[30,32,43].

The mixing of the carbon π orbitals with the orbitals of the heteroatom not only in the "model" compounds, where the atoms of the elements are present as substituents, but also in cyclic compounds—π-donors, benzenes incorporating a non-carbon element in the ring, and the corresponding heterocycles—is analysed in this review.

II. THE π-ORBITALS OF BENZENE AND POLYCYCLIC AROMATIC HYDROCARBONS

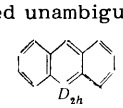
The molecular π orbitals of benzene have been thoroughly investigated and their structures were partly discussed above. The ionisation of degenerate $1e_{1g}$-π orbitals is observed at 9.24 eV, the ionisation of the highest-energy σ orbital is observed at 11.44 eV, and finally the ionisation of the lowest π orbital ($1a_{2u}$) is observed at 12.23 eV.[43] This assignment has been confirmed by the "perfluoro-effect"[44,45]: on passing from an unsaturated or aromatic compound to its perfluoroanalogue, the energies of the π orbitals change slightly, while the energies of the σ orbitals diminish appreciably, which can be seen from the ionisation potentials of hexafluorobenzene[45]: 10.12 eV (π_2, π_3); 12.73 eV (π_1); 14.02 eV (σ).

It has been shown for naphthalene[45] with the aid of the "perfluoro-effect" that a band in the PES beginning at 11 eV corresponds to the ionisation of its σ orbital; the bands in the region of lower energies refer to the ionisation of the π orbitals. This conclusion is in good agreement with the results of a non-empirical calculation according to which the four highest molecular orbitals of naphthalene are π orbitals and the fifth is a σ orbital. The same conclusion has been reached with the aid of calculations by the Hückel molecular orbital method using a parametrisation based on PES data[51-55]; the ionisation potentials (eV) and their assignments are listed below:



D_{2h} 8.12 ($1a_u$) 8.91 ($2b_{1u}$) 10.08 ($1b_{3g}$) 10.85 ($1b_{2g}$) 11.05 ($1b_{1u}$).

The dependence of the structure of the molecular orbitals of polycyclic aromatic hydrocarbons on the number of benzene rings has been investigated with the aid of various quantum-chemical methods and PES data[49,56-59]. It has been established that the energy of the σ orbital of benzene, corresponding to an ionisation energy of 11.44 eV in the PES, becomes 11.00 eV on passing to naphthalene and then does not change appreciably with increase of the number of condensed benzene rings. Therefore all the bands below 11.00 eV, for example in the PES of anthracene and phenanthrene, are assigned unambiguously to the ionisation of π orbitals:



D_{2h} 7.47 ($2b_{2g}$) 8.57 ($2b_{3g}$) 9.23 ($1a_u$) 10.26 ($1b_{2g}$) 10.40 ($2b_{1u}$).

The simple Hückel molecular orbital (HMO) method also yields satisfactory results for large polycyclic aromatic hydrocarbons: in particular, the vertical ionisation potentials I_i of polycyclic aromatic hydrocarbons determined from the PES correspond satisfactorily to the energies ε_i of the π orbitals calculated in units of β in terms of the HMO scheme:

$$I_i = -(\alpha_c + \varepsilon_i \beta_{cc}).$$

This makes it possible to determine the absolute values of the Coulombic integral α_C (within the framework of the simple method, the parameter α_C is identical with the diagonal element H_C) and the resonance integral β_{CC} (the integral β_{CC} is identical with the non-diagonal element H_{CC})[49]:

$$\alpha_c = H_c = -(6.55 \pm 0.34) \text{ eV},$$
$$\beta_{cc} = H_{cc} = -(2.73 \pm 0.33) \text{ eV}.$$

These values are convenient for simple quantum-chemical calculations of the energies of the π orbitals of aromatic hydrocarbons and their heterocyclic analogues[49,50,58,60].

III. CHARACTERISTIC FEATURES OF THE MIXING OF THE ORBITALS OF THE ATOMS OF GROUP II–VII ELEMENTS WITH THE π ORBITALS OF CARBON ATOMS

1. Halogen Atoms

The ionisation potentials of the *p* electrons of the halogen atoms are comparatively high. For example, the following values of *I* (eV) have been found from the PES of hydrogen halides: 16.03–16.06 for fluorine[61]; 12.74–12.82 for chlorine[62]; 11.64–11.98 for bromine[63]; 10.38–11.05 for iodine[62]. The ionisation energies of the unshared electrons of the halogens in halogenomethanes are somewhat lower and are listed in Table 1. This feature of the halogens is reflected in their higher electronegativity compared with carbon and hydrogen atoms[64].

Table 1. Estimation of the degrees of mixing of the *p* (halogen) and benzene π orbitals in the halogenobenzenes PhE.

E	*I*(E), eV	*I*(PhE), eV	$H_{E\pi(sym)}$, eV	Characteristics of the HOMO of PhE*					U.v. spectrum** (Ref.69)
				ε, eV	c_{ortho}	c_{meta}	c_{para}	c_E	
F	14.57 (Ref.52)	9.11 (b_1); 9.82 (a_2); 12.12 (b_1); 12.15 (Ref.67)	−0.84	−9.12	−0.311	0.269	0.566	0.150	210 (3.93); 261 (2.30)
Cl	11.28 (Ref.66)	9.06 (b_1); 9.69 (a_2); 11.32 (b_2); 11.70 (b_1) (Ref.67)	−0.63	−9.07	−0.313	0.256	0.550	0.270	210 (3.88); 257 (2.33)
Br	10.53; 10.86 (Ref.66)	8.99 (b_1); 9.67 (a_2); 10.61 (b_2); 11.18 (b_1) (Ref.68)	−0.62	−9.01	−0.314	0.239	0.530	0.367	204 (3.79); 254 (2.95)
I	9.54; 10.16 (Ref.66)	8.78 (b_1); 9.75 (a_2); 10.59; 11.70 (Ref.8)	−0.59	−8.80	−0.300	0.186	0.453	0.600	207 (3.86); 226 (4.12); 257 (2.85)

Note: *I*(E) are the ionisation potentials of the electrons of the *p*(E) orbital in the halogenomethanes MeE (according to PES data) and *I*(PhE) are the ionisation potentials of the halogenobenzenes (according to PES data).

* The characteristics of the HOMO of the halogenobenzenes (the energy ε and the coefficients c_μ) were obtained by ourselves as a result of calculation by the Hückel molecular orbital method with PES parametrisation (for the details of the calculation, see the Introduction): $H_C = -6.75$ eV; $H_{CC} = -2.5$ eV.[49].

** The positions of the absorption bands (in nm) are indicated (the logarithms of the molar extinction coefficients are shown in brackets).

Since the *p* orbitals of the fluorine atom ionise at the highest energy, the degree of their mixing with the more readily ionisable π orbitals of carbon in fluorobenzene molecules is not considerable, which constitutes the fundamental basis of the "perfluoro-effect" already mentioned, which

lowers significantly the energies of the σ orbitals and to a lesser extent those of the π orbitals. The *p* electrons of the chlorine, bromine, and iodine atoms ionise more readily, but this does not lead to more effective mixing of their orbitals with the π orbitals of the benzene ring, because the effectiveness of the mixing of the orbitals is determined not only by the difference between their energies and by their symmetry but also by their overlap[65]. Table 1 lists the ionisation potentials of the *p* electrons of the halogen atoms in halogenomethanes, the ionisation potentials of halogenobenzenes, and the positions of the intense long-wavelength absorption bands in the ultraviolet spectra of halogenobenzenes. It also lists the integrals $H_{E\pi(sym)}$ characterising the degree of mixing of the p_π orbitals of the halogens with the $\phi_{\pi(sym)}$ orbital of benzene.

The structure of the $\varphi_{\pi(asym)}$ orbital does not change but it has a lower energy, probably as a consequence of the inductive effect of the halogen.

In full agreement with numerous experimental data, it follows from a comparison of the coefficients of the HOMO of various halogenobenzenes that the halogen atoms are *ortho*, *para*-directing and that the directing effect is more marked for the fluorine atom. Comparison of the integrals $H_{E\pi}$ shows that the fluorine atoms are mixed to the greatest extent with the π orbitals of the benzene ring. However, in conformity with the coefficients c_E, the contribution of the unshared electrons of the halogen to the HOMO of the halogenobenzene increases in the sequence

$$F<Cl<Br<I .$$

The greatest bathochromic shifts are undergone by the absorption bands of benzene in the ultraviolet spectrum of fluorobenzene[69]: an intense long-wavelength absorption band is observed in the spectrum of fluorobenzene at 210 nm instead of 203 nm in the spectrum of benzene. In the ultraviolet spectrum of iodobenzene a new absorption band, compared with other halogenobenzenes, appears at 226 nm, which could be accounted for by the mixing of the $5p_x$ orbital of iodine and the π orbitals of benzene. However, the same band is observed also in the electronic spectrum of the iodide ion: apparently the absorption at 226 nm is a consequence of the local electronic transitions and is not related to the $p-\pi$ conjugation system. We may also note that the diphenyliodonium cation absorbs in the region of 226 nm[69,70] (the ultraviolet spectra of compounds in which the bromine and chlorine atoms are linked to two phenyl groups have been investigated[71-73]).

There exist also other estimates of the orbital interactions in halogenobenzenes[64,74-77]. In particular, the degree of mixing of the orbitals of the halogen atoms with the π orbitals of benzene has been estimated[75] in terms of a less rigorous criterion (compared with the integral $H_{E\pi}$ which we proposed), namely the splitting of the energies of the benzene b_1 and a_2 orbitals (the halogenobenzene and the splitting of the energies of these orbitals are indicated below in eV): fluorobenzene, 0.44; chlorobenzene, 0.57; bromobenzene, 0.64; iodobenzene, 0.71. According to this criterion, the 5*p* orbital of iodine is mixed with benzene orbitals to a greater extent than the 2*p*(F), 3*p*(Cl), and 4*p*(Br) orbitals[75].

2. Atoms of Oxygen Subgroup Elements

As in the fluorine subgroup, an increase of the atomic number of the element in the oxygen subgroup decreases its relative electronegativity. However, in aryl(alkyl) chalcogenides the influence of the steric structure on the conditions governing the mixing of the orbitals is significantly more appreciable (compared with halogenobenzenes). We shall examine as an example how the structure of compounds of the type R_2E varies for different E.

The valence angle in the hydrides H_2E diminishes on passing from oxygen to tellurium: 104.5° for O, 92.2° for S, 91.0° for Se, and 89.5° for Te.[78] In dimethyl chalcogenides Me_2E, the C–E–C valence angles are somewhat greater but the trend in their variation is the same: 111.5° for O,[78] 98.9° for S,[79] 98° for Se,[80] and 93° for Te.[81] The closeness of the C–E–C valence angle in the compounds R_2E to 90° can be used to characterise the deviation of the orbitals of the unshared electron pair from the *p* orbitals of the isolated atoms. Using this estimate, one can assume that in the series of dimethyl chalcogenides only the *p* orbitals of tellurium are hardly mixed with the orbitals of the methyl groups: the C–Te–C angle in dimethyl telluride differs insignificantly from 90°. The character of the unshared electrons of the chalcogen atoms in compounds of the type R_2E can be reliably determined within the framework of the molecular orbital method[30]. It has been found that, of the two pairs of unshared electrons formally not involved in the formation of bonds with the hydrogen atoms (for example in the water molecule), only one cannot mix with the *s* orbitals of the hydrogen atoms as a consequence of symmetry properties (b_1 for the C_{2v} symmetry group). The other orbital has the a_1 symmetry, i.e. the same as in the (+)-combination of the *s* orbitals of the hydrogen atoms and can mix with the latter.

In the dimethyl derivatives of the chalcogens Me_2E not only the $p_x(E)$ orbital but also certain combinations of the atomic orbitals of carbon can have the b_1 symmetry[35]. In these compounds the p_x orbital of the chalcogen is involved in the formation of the molecular orbital localised predominantly on the chalcogen: in the PES of dimethyl chalcogenides, the ionisation bands of the corresponding *p* orbitals of the chalcogens are comparatively narrow (although they are wider than in the PES of the hydrides[3]).

Evidently even wider possibilities for the mixing of the orbitals of the unshared electron pairs of the chalcogens with the orbitals of the substituents appear in the corresponding aromatic derivatives. This is probably why the C–E–C angle in compounds of the type PhEMe is even greater: 120° ± 2° for O,[82] 106° ± 2° for S,[83] 99.6° ± 2.5° for Se,[84] and 101° for Te[85]. The stereoelectronic factor exerts an even greater influence on the structure of the molecular orbitals of these compounds. For example, phenyl(alkyl) chalcogenides can exist in a conformation in which the alkyl group is oriented in the plane of the benzene ring and the p_x orbital exists under the most favourable conditions for mixing with the π orbitals of carbon (the dihedral angle $\phi = 0°$). For these compounds there is a possibility also of a different conformation which is sterically less hindered but is unfavourable from the standpoint of the energy of the $n-\pi$ conjugation. It is a perpendicular conformation in which the orbital of the unshared electrons is located in the plane of the benzene ring and can therefore mix only with the σ(CC) orbitals of the skeleton, while the E–C(H_3) bond is in a plane perpendicular to the benzene ring (the dihedral angle $\phi = 90°$).

The conformational properties of phenyl(alkyl) chalgogenides have been investigated by various methods. We shall note only some studies in which the PES method was used for this purpose. In a number of investigations intrinsic ionisation bands in the PES spectra of phenyl(methyl) chalcogenides were assigned to the "planar" ($\phi = 0°$) and "non-planar" ($\phi = 90°$) conformers[86-91]. On the other hand, the authors[85] assumed that the spectrum of telluroanisole reflects the planar conformation and the conformation with a dihedral angle $\phi \cong 60°$. However, the reliability of the

estimate based on PES data for non-planar conformations differing insignificantly in their energies has been questioned[92]. Overall, the data obtained show that the retention of free rotation of the substituents about the E–R bond in the compounds Ar–E–R does not prevent the mixing of the *p* orbitals of the chalcogens with the π orbitals of benzene.

The relative involvement of the *p*(E) orbitals and the π orbitals in the HOMO of anisole analogues is illustrated by the data in Table 2, which also lists the ionisation potentials of the unshared electron pairs of the chalcogens in the dimethyl chalcogenides Me_2E [they were used to estimate the energies of the p_π(E) orbitals which mix with the π orbitals] and the ionisation potentials of compounds of the type C_6H_5EMe. In order to estimate the integrals $H_{E\pi}$ within the framework of the LCFO-MO scheme, the first ionisation potentials of these compounds were employed.

Table 2. Estimation of the degrees of mixing of the *p* orbitals of Group VIA elements with the benzene π orbitals in the compounds PhEMe.

E	*I*(E), eV	*I*(PhEMe), eV	$H_{E\pi}$, eV	Characteristics of the HOMO of PhEMe*					U.v. spectrum** (Ref.97)
				ε, eV	c_{ortho}	c_{meta}	c_{para}	$c_{E(Me)}$	
O	10.04 (Ref.93)	8.21;9.17;10.76; 12.14;13.67; 15.37; [95] ***	−1.37	−8.33	0.38	−0.15	−0.47	−0.54	220 (3.89); 265 (3.13); 271 (3.30); 278 (3.27)
S	8.67 (Ref.94)	8.07;9.28;10.15 [86] ****	−0.84	−8.16	−0.30	0.10	0.36	0.77	254.5***** (3.99)
Se	8.40 (Ref.35)	7.99;8.29;9.24; 9.81;10.77 [90]	−0.72	−8.07	0.27	−0.08	−0.31	−0.84	250 (3.79); 271 (3.51)
Te	7.89 (Ref.35)	7.6–7.83;9.20; 10.27 [85]	−0.69	−7.70	0.24	−0.05	−0.26	−0.89	223 (3.99); 269 (3.69); 331 (2.84)

Note: *I*(E) are the ionisation potentials of the electrons of the *p*(E) orbital in the compounds Me_2E (according to PES data) and *I*(PhEMe) are the ionisation potentials of organoelemental derivatives of anisoles (according to PES data).

* The characteristics of the HOMO of the organoelemental derivatives of anisoles (the energies ε and the coefficients c_μ) were calculated by the Hückel molecular orbital method with PES parametrisation.

** The positions of the absorption bands (in nm) are indicated (the logarithms of the molar extinction coefficients are shown in brackets).

*** cf. Turner's data[96].

**** cf. the data of Bock et al.[42]

***** The absorption band of thioanisole at 200, 254, and 280 nm are indicated by Rodd[98].

Table 2 shows that in the series O, S, Se, Te the *p*(E) and π orbitals mix to the greatest extent for an element in a Second Period (as for the halogens). The most favourable combination of the above factors determining the degree of mixing of the orbitals is in fact encountered for oxygen. According to calculations by the Hückel molecular orbital method (PES parametrisation), the methoxy-group has the most powerful *ortho,para*-directing effect among other groups of the type EMe. With increase of the atomic number of the element, or with decrease of the ionisation potential of the electrons in the *p* orbital, and with the consequent increase of the difference between the energies of the interacting *p* and π(sym) orbitals, the contribution of the atomic orbitals of the chalcogen to the HOMO of the PhEMe molecule increases in the sequence

$$O<S<Se<Te.$$

On passing from anisole to thioanisole, selenoanisole, and telluroanisole, there is a bathochromic shift of the long-wavelength absorption in the ultraviolet spectra (Table 2). The maximum shift of the intense long-wavelength band is observed in the spectrum of thioanisole. These facts can be partly explained by the increased HOMO energy in the above series of compounds[97,99,100]. There is also a possibility of the involvement of unoccupied *d* orbitals for which the possibilities for mixing with the unoccupied π orbitals of benzene are in fact greatest in the case of the sulphur atom. The absorption bands at 223 and 231 nm, observed in the spectrum of telluroanisole, are apparently determined to a large extent by local effects.

We may also note that there exist other schemes for the parametrisation of the quantum-chemical calculations based on PES data[30,101–108]. In the method for the estimation of the parameters $H_{\mu\nu}$ adopted in this review the influence of the inductive effect of the substituent E on the energies of the benzene π orbitals and the difference between the inductive effects of the methyl and phenyl groups in the estimation of the energies of the atomic orbitals of the elements are not taken into account explicitly. In the parametrisation based on PES data for *p*-disubstituted benzenes, a correction has been made[30] for the alteration of the energy of the *n*(E) orbital as a consequence of the inductive influence of the benzene fragment but no account is taken of the difference between the sensitivities to the inductive effect of the benzene $\varphi\pi$(sym) and $\varphi\pi$(asym) orbitals.

Quantum-chemical studies in terms of the π-approximation, parametrised on the basis of PES data, have been used successfully[109–119] for the analysis of the molecular orbitals also of aromatic organoelemental compounds—monocyclic and polycyclic aromatic compounds containing heteroatoms in the ring. In particular, calculations in terms of the π-approximation were carried out using the parameters (eV)

$$\alpha_S = -9.4;\ \alpha_{Se} = -8.5;\ \alpha_C = -7.0;\ \beta_{CS} = -1.8;\ \beta_{CSe} = -1.5;\ \beta_{CC} = -3.0\ .$$

These made it possible to interpret reliably the PES of furan and its analogues[109,110]. For example, the $3p_\pi$ orbital of the sulphur atom in the thiophen molecule is fully conjugated with the π orbitals of carbon, which results in the formation of delocalised molecular orbitals, and on photoionisation it is not manifested by a separate band in the spectrum: the first two ionisation potentials of 8.9 and 9.5 eV have been attributed to the two highest π-electronic levels: $a_2(\pi)$ and $b_1(\pi)$ respectively. The replacement of the S atom by O, Se, and Te atoms affects only slightly the $a_2(\pi)$ level but alters significantly the energy of the $b_1(\pi)$ level. This type of dependence of the energies of the above molecular orbitals on the nature of the heteroatom can be understood by analysing their symmetries: the energy of the $a_2(\pi)$ molecular orbital, which has a nodal plane passing through the heteroatom, varies less than the energy of the $b_1(\pi)$ orbital to which the orbital of the heteroatom makes a considerable contribution[109,110]. The ionisation potentials (eV) of the a_2 and b_1 orbitals of compounds (I) are presented below:



(I)

	O	S	Se	Te
a_2	8.90	8.87	8.80	8.81
b_1	10.32	9.52	8.95	8.27

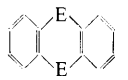
This contribution becomes a maximum for E = Te: the highest occupied orbital of tellurophen is a $b_1(\pi)$ orbital.

The character of the $p(E)-\pi$ mixing in tricyclic compounds is illustrated by the results of a study[119] in which the PES of dibenzofuran analogues were investigated and interpreted. The measured (PES) and calculated (Hückel molecular orbital method, PES parametrisation) ionisation potentials of, for example, dibenzoselenophen, are compared below:

I(exp.), eV	7.88	8.30	9.25	9.95	10.43	11.27	12.93
I(calc.), eV	8.07	8.51	9.25	9.81	10.07	11.47	12.58
Orbital	$5b_2$	$2a_2$	$4b_2$	$3b_2$	$2b_2$	$1a_2$	$1b_2$

Evidently the fragment π orbitals of the benzene nuclei and the p orbitals of the heteroatom are mixed in the molecule of this compound to the same extent as in the model compound: selenoanisole. An analogous conclusion applies also to other dibenzofuran analogues having planar molecules[120-123] and the maximum overlaps of the $p(E)$ and π orbitals. In the ultraviolet spectra of compounds of the dibenzofuran series, the greatest changes in the energies of the electronic transitions are observed on passing from dibenzofuran (absorption maxima at 249, 281, and 297 nm[124]) to dibenzothiophen (absorption maxima at 286, 313, and 323 nm[124]), while the spectra of dibenzoselenophen and dibenzotellurophen[125] are virtually identical with the spectrum of their thio-analogue.

In tricyclic compounds having the general structure

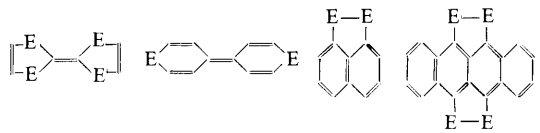


(II)

E = O, S, Se, Te

in the molecules of which the number of π electrons does not satisfy the Hückel rule for aromatic compounds, the p orbitals of the chalcogens and the carbon π orbitals are mixed less effectively. For example, the non-diagonal matrix element $H_{O\pi(asym)}$, found from the PES data for compound (II, E = O) is 0.94 eV, while 1.19 eV has been obtained from the PES of anisole. Although the molecule of dibenzo-p-dioxin is planar in the crystalline state[126], the discrepancies observed for compounds (II) between the measured and calculated ionisation potentials[127-129] can be due to the non-planarity of their molecules in the gas phase[130-132].

Among other compounds in which the chalcogen atoms are part of the composition of rings having more than six p electrons, mention should be made of derivatives of tetrathiafulvalene (III), dithiapyranylidene (IV), naphthalene (V), and tetracene (VI). The interest in the characteristics of the structure of the molecular orbitals of compounds (III)–(VI), in which E = O, S, Se, or Te, can be explained by the fact that the compounds exhibit electron-donating properties in highly conducting complexes with π acceptors[133-137]:



(III) (IV) (V) (VI)

In particular the PES of tetrathio-, dithiodiseleno-, and tetraseleno-fulvalenes, (IIIa), (IIIb), and (IIIc), respectively have been investigated[135]. In the region of low ionisation energies (below 11 eV), all three compounds have virtually identical PES: the replacement of the S atom by Se does not invert the sequence of the molecular orbitals. It is significant that the energies of all the π orbitals, except the HOMO, increase somewhat on successive replacement of the sulphur atoms by selenium. On the other hand, the energy of the HOMO, which is the most delocalised orbital, decreases somewhat [the first ionisation potentials of the compounds (IIIa), (IIIb), and (IIIc) are respectively 6.70, 6.75, and 6.90 eV].

Interesting results have been obtained by the LCFO-MO method in the analysis of the orbital interactions in naphthalene 1,8-disulphide (V).[136] The occupied molecular π orbitals of the compound are produced from the corresponding orbitals of two fragments—the naphthalene molecule and the disulphide bridge. The following molecular orbitals were taken into account for the naphthalene fragment (symmetry group approximately C_{2v})[45]: a_2 (−8.13 eV); b_1 (−8.88 eV); b_1 (−10.01 eV); a_2 (−11.37 eV); b_1 (−13.0 eV). The interaction between the p_π orbitals of two neighbouring sulphur atoms leads to two new energy levels [−8.1 (a_2) and −10.1 (b_1) eV] to which correspond wave function in the form of linear $p(-)$ and $p(+)$ combinations[138,139]. The determination of the energies of the molecular orbitals of naphthalene 1,8-disulphide reduces to the solution of two secular equations set up respectively for the a_2 and b_1 orbitals. The diagonal matrix elements $H_{\mu\mu}$ are set equal to the energies of the basis fragment orbitals (FO) and the non-diagonal matrix elements are found from the relation

$$H_{\mu\nu} = \sqrt{2} \cdot C_\mu \beta_{CS},$$

where C_μ is the coefficient of the molecular orbital of naphthalene at the site of the addition of the disulphide bridge (for the 1- and 8-positions, the values of C_μ are identical and for the four occupied molecular orbitals enumerated above they amount to 0.425, 0, 0.263, and 0.301 respectively) and β_{CS} is the integral characterising the interaction of the $2p(C)$ and $3p(S)$ orbitals; $\beta_{CS} = -1.8$ eV has been adopted[140]. The corresponding secular equations in the case under consideration have the following form:

$$\begin{vmatrix} (-8.13-\varepsilon) & 0.60\beta_{CS} & 0 \\ 0.60\beta_{CS} & (-8.10-\varepsilon) & 0.37\beta_{CS} \\ 0 & 0.37\beta_{CS} & (-11.37-\varepsilon) \end{vmatrix} = 0;$$

$$\begin{vmatrix} (-10.01-\varepsilon) & 0.57\beta_{CS} & 0 \\ 0.57\beta_{CS} & (-10.1-\varepsilon) & 0.43\beta_{CS} \\ 0 & 0.43\beta_{CS} & (-13.80-\varepsilon) \end{vmatrix} = 0.$$

Calculated data agree very well with experimental results.

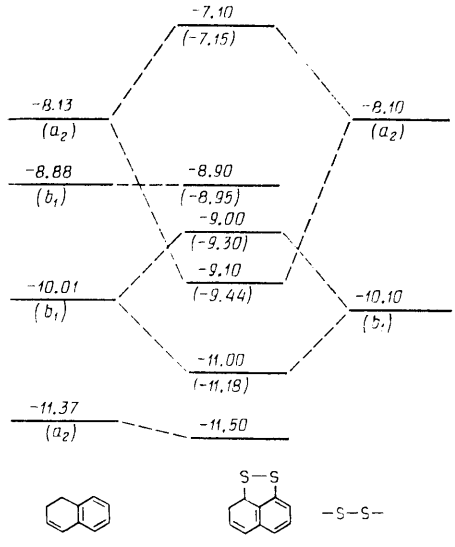


Figure 1. Schematic illustration of the formation of the π orbitals of 1,8-naphthylene disulphide[136] (the energies are indicated in electron-volts).

Fig. 1 illustrates a qualitative diagram describing the distribution of the π orbitals with respect of energy in the naphthalene 1,8-disulphide molecule (the estimated molecular orbital energies are indicated: the values based on PES data in brackets and the calculated values without brackets).

In conclusion of the discussion of the characteristics of the formation of the molecular orbitals from the fragment p(E) and π orbitals in compounds of Group VIA elements, we may note that, although the degree of mixing of the fragment orbitals decreases in the sequence O > S > Se > Te, selenium compounds and in certain cases also tellurium compounds have been found to be the most promising π donors in the corresponding complexes of organic metals[141,142].

3. The Atoms of Nitrogen-Subgroup Elements

In contrast to dimethyl chalcogenides Me_2E, in the series of compounds Me_3E (where E = N, P, As, or Sb) the increase of the atomic number and the decrease of the electronegativity of the element E never lead to a decrease of the ionisation potentials of its unshared electrons: the ionisation potentials of trimethylamine, trimethylphosphine, and trimethylarsine are almost identical (a slight increase is actually observed on passing from nitrogen to arsenic)[143]. The ionisation potentials of the unshared electron pairs of the heteroatoms in the hydrides H_3E differ to a greater extent[144]; The corresponding data are presented in Table 3.

Table 3. Estimation of the degrees of mixing of the n orbitals of Group VA elements with the benzene π orbitals in the compounds $PhEMe_2$.

E	I(E), eV* (Ref.143)	I($PhEMe_2$), eV	H_{Em}, eV	Characteristics of the HOMO of $PhEMe_2$*					U.v. spectrum** (Ref.149)
				ε, eV	c_{ortho}	c_{meta}	c_{para}	c_E(Me_2)	
N	8.50	7.6;9.2;10.0 [146]	−1.21	−7.82	−0.36	0.08	0.39	0.72	251 (4.15); 299 (3.31)
P	8.60	8.45 (n); 9.2 (a_2+b_1) [146]	−0.34	−8.47	−0.18	0.08	0.23	0.91	251 (3.54)
As	8.65	8.67 (n); 9.31 (a_2+b_1); 10.7—11.0 [148]	0.0	—	—	—	—	—	241.5 (3.83)
Sb	8.48	—		—	—	—	—	—	250 (2.57)

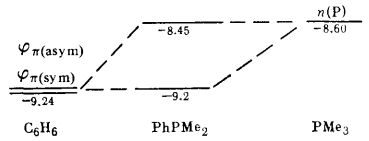
Note: I(E) are the ionisation potentials of the electrons in the n(E) orbital in the compounds Me_2E (according to PES data) and I($PhEMe_2$) are the ionisation potentials of the analogues of *N,N*-dimethylaniline (according to PES data).

* The characteristics of the HOMO of the compounds $PhEMe_2$ (the energies ε and the coefficients c_μ) were calculated by the Hückel molecular orbital method with PES parametrisation (for the details of the calculations, see the Introduction).

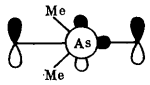
** The positions of the absorption bands (in nm) are indicated (the logarithms of the molar extinction coefficients are shown in brackets).

In analysing this feature of compounds of Group VA elements, one must bear in mind the variation of the geometry, in particular in the series of compounds Me_3E and the corresponding variation of the hybridisation of the orbital of the unshared electrons of the heteroatom: for example, the C—E—C angle decreases from 108° for NMe_3 to 99° for PMe_3 and 96° for $SbMe_3$. According to Walsh[145], the increase of the deviation from the planar structure on passing from nitrogen to antimony corresponds to an appreciable alteration of the hybridisation of the orbital of the unshared electrons, to an increase of its s character, and to the corresponding decrease of its energy. Such hybrid orbitals of the unshared electrons of Group V elements would apparently be more correctly designated by the letter n rather than p.

It appears that the mixing of the n orbital with the π orbitals of the corresponding benzene derivatives $PhEMe_2$ depends primarily on the degree of hybridisation of the n orbital[146,147]. In contrast to *N,N*-dimethylaniline, in the molecule of which the n orbitals of nitrogen and the orbitals of carbon are actively mixed, in *P,P*-dimethylphenylphosphine the degree of n(P)−π mixing is much lower[146] (Table 3):



The conformations and PES of dimethylvinyl- and dimethylphenyl-arsines have been investigated[148]. In these compounds the n(As) and π orbitals are not mixed; the first ionisation potentials of trimethylarsine and dimethylphenylarsine are almost identical, amounting to 8.65 and 8.67 eV respectively. It is of interest to note that the calculation by the CNDO/2 method for dimethylphenylarsine showed that the optimum conformation is one in which the n orbital of the arsenic atom, the bisector of the Me—As—Me angle, and the benzene ring are located in a single plane:



This conclusion is not unexpected: the same conformation had been observed earlier in solution for dialkyl(*p*-tolyl)-phosphines[150]. On the other hand, consistent with the assumption made, the *N,N*-dimethylaniline molecule has a conformation favourable for the n(N)−π conjugation: the $PhNC_2$ fragment is almost planar—the average C—N—C angle is 116°.[151] In this connection we may note that the effect of the n(P)−π conjugation in the series of compounds of tricoordinate phosphorus and its analogues have been investigated in detail also by other methods, in particular by potentiometric titration[152].

Table 4. The ionisation potentials (I, eV) of the compounds Ph_3E according to PES data[154].

E	I_1	I_2	I_3	I_4
N	7.00	8.81	9.25	10.29
P	7.85	9.02	9.18	9.68
As	8.03	—	9.10	9.58
Sb	8.08	—	9.06	—

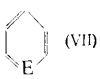
The formation of the molecular orbitals of triphenylamine and its analogues of the type Ph_3E has been investigated[153,154]. Table 4 lists the vertical ionisation potentials of Ph_3E, which lie below 11 eV.[154] The ionisation potentials at 9 eV (I_2 and I_3) were attributed to orbitals localised preferentially in the

benzene rings; the ionisation potentials I_1 and I_4 were assigned to the orbitals formed by the mixing of the benzene π orbitals and the orbitals of the unshared electrons of the heteroatom. The maximum mixing of the n(E) and carbon π orbitals is observed in triphenylamine: the PES of this compound does not reveal the ionisation of isolated n(N) and π orbitals. The first band in the PES, characterising the n(E)$-\pi$ mixing, becomes narrower on passing from N to P and further to As and Sb.[153] As in the series of compounds $PhEMe_2$, in the present series of compounds the degree of n(E)$-\pi$ mixing diminishes sharply on passing from N to P and falls still further on transition to As and Sb:

$$N \gg P > As > Sb .$$

The PES data for p-disubstituted benzenes described by the formula p-$Me_2EC_6H_4EMe_2$ are fully consistent with the conclusion that the degrees of n(E)$-\pi$ mixing in the nitrogen and phosphorus compounds are significantly different[147].

However, it must be emphasised yet again that the weak capacity of the n orbital of the tricoordinate phosphorus atom (and also arsenic and antimony atoms) for mixing with the π orbitals is caused by the characteristics of its hybridisation. The alternative explanation of the above phenomenon, based on geometrical causes [the difference between the effective dimensions of the 3p(P) and 2p(C) orbitals, the greater E–C bond length compared with the N–C bond length, etc.], is hardly likely to be valid, because heteroaromatic compounds with dicoordinate atoms of Group VA elements, up to bismuthabenzene, are known:



(VII)

E=N, P, As, Sb, Bi .

The steric and electronic structures of organoelemental derivatives of benzene of type (VII) have been studied in detail and discussed in a number of reviews[48,155]. In the present review we shall confine ourselves to the principal conclusions reached in the investigations concerning the comparative estimates of the degrees of mixing of orbitals of different elements.

The molecules of compounds (VII) are planar and their bond lengths are characteristic of aromatic compounds. For example, according to the data of Bart and Dely[156], the phosphorus–carbon bond length in 2,6-dimethyl-4-phenylphosphabenzene is 1.74 Å, while the length of the P=C double bond in the $Ph_3P{=}CH_2$ is 1.65 Å and that of the P–C single bond in trimethylphosphine is 1.87 Å. The carbon–nitrogen, carbon–arsenic, and carbon–antimony bond lengths in the corresponding organoelemental derivative of benzene are 1.37 Å,[157] 1.85 Å,[158] and 2.05 Å.[159]

The principal spectroscopic characteristics of the organoelemental derivatives of benzene (VII) are listed in Table 5. The structure of the occupied molecular orbitals in these compounds can be naturally accounted for within the framework of the simple molecular orbital perturbation scheme (theory)[160]: the changes in the energy levels of the benzene π orbitals are determined by the coefficients of these orbitals referring to the position of the heteroatom. In conformity with the squares of these coefficients for the π orbitals of benzene (0.33 for $2b_1$, 0 for a_2, and 0.17 for $1b_1$), the greatest changes following the introduction of the heteroatom are undergone by the ionisation potential of the φ_π(sym) orbital (the $2b_1$ orbital); the energy of the π_1 orbital (the $1b_1$ orbital) changes less and finally the energy of the φ_π φ_π(asym) orbital (the a_2 orbital) hardly changes when the CH fragment is replaced by a heteroatom. We may note that there are linear relations between the ionisation potentials of the π orbitals of compounds (VII) and the ionisation potentials I_E of the p orbitals of the elements[160]:

$$I_{(2b_1)} = (5.24 + 0.36I_E), \text{ eV} \quad (r = 0.9998) ;$$
$$I_{(1b_1)} = (10.25 + 0.16I_E), \text{ eV} \quad (r = 0.9908).$$

(The values of I_E are 14.53 eV for N, 11.0 eV for P, 9.81 eV for As, and 8.64 eV for Sb.)

Table 5. The spectroscopic characteristics of organoelemental derivatives of benzenes PhE (E is a Group VA element).

E	I(PhE)*, eV (Ref.160)	U.v. spectrum** (Refs. 17, 161)
N	9.7–9.8 ($11a_1$, σ/n; $1a_2$, π), 10.5 ($2b_1$, π); 12.5 ($7b_2$, σ); 12.6 ($1b_1$, π)	175 (4.90); 192 (3.80); 250 (3.30) 270 (2.65)
P	9.2 ($3b_1$, π); 9.8–10.0 ($1a_2$, π; $13a_1$, σ/n); 11.5 ($8b_2$, σ); 12.1 ($2b_1$, π)	213 (4.28); 246 (3.93); 290 sm. (2.40)
As	8.8 ($5b_1$, π); 9.6–9.9 ($2a_2$, π; $17a_1$, σ/n); 11.0 ($10b_2\sigma$); 11.8 ($4b_1$, π)	219 (4.18); 268 (4.04); 305 sm. (2.54)
Sb	8.3 ($7b_1$, π); 9.4–9.6 ($3a_2$, π; $21a_1$, σ/π); 10.4 ($12b_2$, σ); 11.7 ($6b_1$, π)	236; 312

* The ionisation potentials of organoelemental derivatives of benzene (according to PES data).
** The positions of the absorption bands (in nm) are indicated (the logarithms of the molar extinction coefficients are shown in brackets); the solvent was cyclohexane.

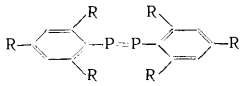
The analysis of the structure of the occupied molecular orbitals of the organoelemental derivatives of benzene (VII) described above has been justified[160] with the aid of an *ab initio* calculation for phosphabenzene whereby it was found that none of the occupied molecular orbitals of this compound contains an appreciable contribution of the unoccupied 3d(P) orbitals (there exists also a different view concerning the role of these orbitals in the formation of the molecular orbitals of phosphabenzene[162]).

It is of interest to compare the fact of the active involvement of the p(E) orbitals in the formation of the π-type molecular orbitals of organoelemental benzene derivatives with data concerning the character of the orbitals of the unshared electrons of the heteroatoms in these heterocycles: the ionisation of the unshared electrons is manifested in the PES of both the hydrides H_3E and organoelemental benzene derivatives in the region of 10 eV, but the corresponding bands in the spectrum are overlapped by the band due to the ionisation of the benzene π orbitals[160,163–165]. The ionisation of the unshared electrons of the sp^2-hybridised phosphorus atom was first observed in the form of an individual band by Schäfer et al.[164]; the band half-width in the PES of 2-phosphanaphthalene proved to be only 20% smaller than the half-width of the band due to the ionisation of the unshared electrons of the sp^3-hybridised phosphorus atom. The n orbital of the phosphorus atom, located in the plane of the carbon fragment in the molecules of aromatic phosphorus compounds (phosphabenzene, phosphanaphthalene, and phospha-anthracene), is apparently mixed with the σ(CC) orbitals.

The capacity of the 3p(P) orbitals for appreciable overlapping with the 2p(C) orbitals had been observed earlier in linear compounds, in particular in coloured compounds of the type of cyanines and triarylmethanes[166–169]: X-ray diffraction studies showed, for example, that the phosphorus–carbon bond length in phosphamethinecyanines is

1.76 Å[168,169], i.e. is virtually the same as in phosphabenzene (1.74 Å).

The geometrical parameters of the *p* orbitals of the elements of high Periods do not prevent their overlap with both the π orbitals of the sp^2-hybridised carbon atom and with the *p*(E) orbital of another E atom. Bis(2,4,6-tri-t-butylphenyl)diphosphene, the first stable compound with a double bond between phosphorus atoms, has been recently isolated and characterised[170] (cf. the earlier communications[171-173]):



(VIII)

R = t-Bu .

The molecule of the diphosphene (VIII) is planar and the P=P bond length is 2.034 Å; its ultraviolet spectrum [284 (ε = 15660), 340 (ε = 7690), and 460 (ε = 1360)] resembles very closely that of its *N*-analogue—bis(2,4,6-tri-t-butylphenyl)diazene[174].

4. The Atoms of Carbon Subgroup Elements

We shall now discuss the behaviour of the benzene π orbitals under the influence of substituents incorporating atoms of the Group IVA elements. In the sp^3 valence state these elements form bonds assuming tetrahedral directions and have comparatively low ionisation potentials. In the corresponding non-planar compounds the σ and π orbitals of the individual fragments are therefore capable of mixing, although, for example, in compounds having the general structure $PhEMe_3$, the perturbation of the benzene π orbitals is slight: the first ionisation potential decreases by only 0.24 eV on passing from benzene to trimethylphenylsilane.

The interaction of the π orbitals of the benzene ring with the orbitals of the σ(E—C) bonds in the compound $PhEMe_3$ has been discussed in detail in many communications; certain questions concerning this problem were considered above (in the introduction).

In the series of compounds $PhEMe_3$, one is dealing with the possibility of the mixing of the benzene $\varphi\pi$(sym) and σ(E—Me) orbitals[37]. The ionisation potential of the electrons of the σ(E—C) orbitals in the series of compounds Me_4E varies in parallel with the variation of the electronegativity of the element E[175]. However, one should note that the first ionisation potentials of the compounds $PhEMe_3$ vary only slightly: the degree of mixing of the σ(E—C) and π orbitals in the phenyl derivatives of the elements of the carbon subgroup as well as the degree of mixing of the *n*(E) and π orbitals in the corresponding compounds of Group V—VII elements decrease with increasing atomic number of the element:

$$C > Si > Ge > Sn .$$

The corresponding data, including the results of quantum-chemical calculations for the compounds $PhEMe_3$ in terms of the π-approximation (parametrisation based on PES), are presented in Table 6.

It is noteworthy that the longest-wavelength absorption is observed in the ultraviolet spectra of phenylsilanes. The maximum shift of the absorption band has been observed in

Table 6. Estimation of the degrees of mixing of the σ(E—C) and σ(C—E) orbitals with the benzene π orbitals in the compounds $PhCH_2EMe_3$ and $PhEMe_3$.

E	*I*(E-C), eV	Ionisation potential*, eV (Ref.43)	*H*(EC), eV	Characteristics of HOMO**					U.v. spectrum**** (Ref.177)
				ε, eV	c_{ortho}	c_{meta}	c_{para}	c(EC)***	
				$PhEMe_3$					
C (IX)	11.4	8.83 (π_2); 9.31 (π_3); 10.92; 11.39 (σ (CC)); 12.11 (π_1); 12.72; 12.93; 14.93	−1.03	−8.85	−0.34	0.22	0.53	0.36	208 (3.93); 258 (2.30)
Si (X)	10.5	9.00 (π_2); 9.26 (π_3); 10.48—10.60 (σ (SiC); 11.56; 11.91 (π_2) [176]	−0.60	−9.01	−0.31	0.24	0.53	0.37	211 (4.03); 260 (2.48)
Ge (XI)	10.2	9.00 (π_2); 9.25 (π_3); 9.98—10.30 (σ (GeC); 11.63 (σ (CC)); 11.97 (π_1); 12.80; 13.91	−0.54	−9.01	−0.31	0.23	0.52	0.41	208 (4.08); 258 (2.30)
Sn (XII)	9.7	8.94 (π_2); 9.29 (π_3); 9.71—10.02 (σ (SnC); 11.58 (σ (CC); 12.02 (π_1); 12.72; 13.87	−0.48	−8.95	−0.30	0.21	0.48	0.53	209 (4.09); 252 (2.78)
				$PhCH_2EMe_3$					
C (XIII)	11.4	8.77 (π_2); 9.13 (π_3); 10.73; 11.41 (σ (CC)); 12.10 (π_1); 12.49; 13.81	−1.21	−8.73	−0.36	0.21	0.52	0.39	211 (4.67); 259 (2.24)
Si (XIV)	10.5	8.42 (π_2); 9.08 (π_3); 10.53 (σ (C Si); 11.40 (σ (CC)); 11.98 (π_1); 12.78; 13.55	−1.33	−8.48	−0.37	0.17	0.49	0.49	222 (3.94); 267 (2.63)
Ge (XV)	10.2	8.40 (π_2); 9.12 (π_3); 10.41 (σ (CGe)); 11.43 (σ (CC)); 12.01 (π_1); 12.92; 13.67	−1.39	−8.36	−0.38	0.15	0.48	0.52	225 (3.86); 269 (2.53)
Sn (XVI)	9.7	8.21 (π_2); 9.21 (π_3); 9.90—10.32 (σ (CSn); 11.42 (σ (CC)); 11.99 (π_1); 12.83,13.25	−1.35	−8.24	−0.38	0.14	0.46	0.58	236 (3.74); 272 (2.69)

Note: *I*(E—C) are the ionisation potentials of the σ(E—C) orbitals in the compounds Me_4E (according to PES data).

* The ionisation potentials of the compounds $PhEMe_3$ and $PhCH_2EMe_3$ are indicated (according to PES data).

** The characteristics of the HOMO of the compounds $PhEMe_3$ and $PhCH_2EMe_3$ (the energies ε and the coefficient c_μ were obtained by ourselves from calculations by the Hückel molecular orbital method with PES parametrisation (see the Introduction for the details of the calculations).

*** The coefficient c(CE) are indicated for the compounds $PhCH_2EMe_3$.

**** The positions of the absorption bands in nm are indicated (the logarithms of the molar extinction coefficients are given in brackets).

the ultraviolet spectrum of *p*-bis(trimethylsilyl)benzene [absorption bands at 226 and 270 nm compared with the bands at 214 and 263 nm in the ultraviolet spectrum of *p*-bis(t-butyl)benzene].[178] This feature is probably due to the contribution of the unoccupied 3*d* orbitals of silicon to the unoccupied molecular orbitals of phenylsilanes, which reduces the energies of these molecular orbitals. The molecular orbital perturbation theory[43] and the CNDO/2 method (both with and without the inclusion of the 3*d* orbitals in the basis set)[179] have been used for quantitative estimates of the contributions of the 3*d*(Si) orbitals.

Since the unoccupied d_{xz} orbitals of silicon have b_1 symmetry (relative to the C_{2v} group, they can be mixed also with the occupied σ and π orbitals of benzene having the same symmetry, which decreases the energy levels of the corresponding HOMO and hence also the absolute value of the integral $H_{\sigma\pi}$ characterising the degree of σ–π mixing in the compounds $PhEMe_3$. Furthermore, the low degree of mixing of the π and σ(E–C) orbitals in the series of compounds (X)–(XII) can probably be explained also by the fact that the C_{ar}–E(Me) bond length increases on passing from Si to Sn, which hinders the mixing.

A more objective estimate of the capacity of various σ(C–E) orbitals for mixing is possible on comparing the corresponding spectroscopic characteristics of the benzyl derivatives $PhCH_2EMe_3$: in these compounds the C_{ar}–C(E) bond length is independent of E and the capacity for overlap of the *d* orbitals of the element with the benzene π orbitals is also significantly reduced. The ionisation potentials measured by the PES method[43,180], the results of quantum-chemical estimations, and the positions of the long-wavelength absorption bands in the ultraviolet spectra of the compounds $PhCH_2EMe_3$ are also presented in Table 6. As was to be expected, the degree of mixing of the σ(C–E) and π orbitals in these compounds is determined mainly by the difference between their energies and is therefore a maximum for the σ(C–Ge) and σ(C–Sn) orbitals.

The results presented in Table 6 agree well with the experimental data[37] and with the estimates[180] of other workers. Here it is appropriate to mention the results obtained when account is taken of contributions of different kinds to the observed changes in the energies of the highest occupied molecular orbitals. In particular, the results of such analysis have been obtained for the phenyl and benzyl derivatives of Group IVA elements $PhEMe_3$ and $PhCH_2EMe_3$.[43] Within the framework of molecular orbital perturbation theory, the changes in the energies of the benzene π_1 and $\pi_{2(sym)}$ orbitals δE_{π_1} and δE_{π_2} can be represented as the sums of the inductive ($q_{\mu i}.\delta W_i$) and hyperconjugation ($\beta^2 q_{\mu i}\Delta E^{-1}$) contributions:

$$\delta E_{\pi_1} = (1/6)\,\delta W + (1/6)\beta^2 (E_{\pi_1} - E_\sigma)^{-1},$$
$$\delta E_{\pi_2} = (1/3)\,\delta W + (1/3)\beta^2 (E_{\pi_2} - E_\sigma)^{-1},$$

while the change in the energy of the σ(E–C) orbital is defined by the formula

$$\delta E_\sigma = (1/3)\beta^2 (E_\sigma - E_{\pi_2})^{-1} + (1/6)\beta^2 (E_\sigma - E_{\pi_1})^{-1}.$$

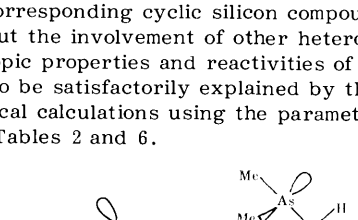
In these expressions E_σ, E_{π_1}, and E_{π_2} are the energies of the corresponding unperturbed orbitals, $q_{\mu i}$ is the electron density of the φ_μ orbital at the *i*th centre, δW_i is the change of the effective ionisation potential of the *i*th carbon atom as a consequence of the inductive effect of the substituent, and β is the resonance integral between the 2*p*(C) orbital of the *i*th atom and the orbital of the substituent. The electron-accepting influence of the unoccupied *d* orbitals has been estimated by comparing the calculated and experimental estimates of δE_{π_2}. Table 7 summarises the results obtained. The determination of the contributions of the individual components enumerated in Table 7 is based on the experimental estimates of δE_{π_1}, δE_{π_2}, and δE_σ. The accuracy of such estimates is low and they must be regarded as extremely approximate; in particular, unstructured bands in the PES correspond to the ionisation of the σ orbitals. This is possibly why the hyperconjugation contributions by the carbon–element bonds in the benzyl compounds have been found to be clearly too low: they proved to be smaller even than the inductive contributions and also the corresponding contributions in compounds of the type $PhEMe_3$. Such results conflict with the estimates of other authors and the experimental data[37,180]. The effects of the mixing of the σ and π orbitals have also been investigated for the corresponding allyl compounds[180]. It is of interest that here the authors concluded that the resonance integrals β for the π and σ(C–E) orbitals are constant (for different E).

Table 7. Analysis of the causes of the changes in the orbital energies in the compounds $PhEMe_3$ and $PhCH_2EMe_3$ (according to the data of Dewar et al.[43]).

Compound	Contributions to δE_{π_2}, eV				Contributions to δE_{π_1}, eV		
	inductive	hyperconjugation	p_π–d_π	sum	inductive	hyperconjugation	sum
(X)	0.78	0.51	–1.09	0.20	0.39	–0.12	0.27
(XI)	0.64	0.38	–0.82	0.20	0.32	–0.06	0.26
(XII)	0.48	0.34	–0.51	0.31	0.24	–0.03	0.21
(XIV)	0.30	0.10* (0.7)	—	0.40	0.15	–0.05	0.10
(XV)	0.28	0.14* (0.9)	—	0.42	0.14	–0.07	0.07
(XVI)	0.38	0.23* (1.0)	—	0.61	0.19	–0.10	0.09

* Estimates of the hyperconjugation effect based on the data of Schweig et al.[180] are presented in brackets for comparison.

Among other types of organic compounds of Group IVA elements, in which the σ and π orbitals are mixed, one should mention arylpolysilanes[181–183]. Estimates of the degree of σ(Si–Si)–π mixing in their molecules have been obtained from PES data and the absorption spectra of charge-transfer complexes and the influence of the stereoelectronic factor has been revised[184]. The σ(Si–C) and π orbitals are also mixed in the corresponding cyclic silicon compounds both with and without the involvement of other heteroatoms[176,185]. The spectroscopic properties and reactivities of these compounds can also be satisfactorily explained by the results of quantum-chemical calculations using the parameters enumerated above in Tables 2 and 6.



The σ–π mixing is undoubtedly not a specific feature of organic compounds of Group IVA elements. For example, it also occurs in allyl sulphides[186]. The dependence of the degree of mixing of the σ(C–As) and π orbitals on the conformation has been studied[148]. It has been found that these orbitals are not mixed in benzyldimethylarsine, but their contribution to the HOMO of allyldimethylarsine, which has a different conformation, is extremely significant.

As for the atoms of Group VA elements, the 3*p* orbital of the silicon atom can be mixed with the carbon π orbitals to form molecular orbitals of the corresponding aromatic compounds. Among such compounds, mention should be made in the first place of silabenzene and silatoluene—compounds in which the silicon atom is in a tricoordinate state and which exhibit properties characteristic of aromatic compounds. Owing to their exceptionally high reactivity, it was for a long time not only impossible to isolate silabenzene and silatoluene in a pure state and to investigate them using appropriate chemical reactions but it was actually not possible to detect them by employing "trapping" reactions[17]. However, theoretical calculation showed that silabenzene should be thermodynamically very stable. In particular, it followed from the MINDO/3 calculation that the C—Si bond length of the cyclobenzene molecule should be 1.753 Å, which is ~ 5% less than the length of the C—Si single bond in methylsilane (1.837 Å).[187] According to the results of the *ab initio* calculation (in terms of the STO-3G basis set), the conjugation energy in the silabenzene molecule is −22 kcal mol^{-1} (for the benzene molecule the calculated conjugation energy is −32 kcal mol^{-1} and agrees fully with experimental data).[188]

The somewhat more stable silatoluene had been obtained earlier by the dehydrochlorination (at −77 °C) of 1-chloro-1-methyl-1-silacyclohexa-2,4-diene[189] and the pyrolysis (at 450 °C) of 1-allyl-1-methyl-1-silacyclohexa-2,4-diene[190]. Silabenzene was obtained in 1980 by the pyrolysis of 1-allyl- and 1-acetoxy-1-silacyclohexa-2,4-dienes[191,192].

The published PES of these aromatic organosilicon compounds are of interest. In conformity with the relations noted above and found in a study of the PES of phosphabenzene and its analogues, the ionisation potentials of silabenzene should vary linearly with the ionisation potential of the 3*p* electrons of the silicon atom. The calculated ionisation potential of silabenzene and its value determined from the PES are similar:

I(calc.), eV (Ref.1)	8.2 ($\varphi_{\pi(\mathrm{sym})}$)	9.2 ($\varphi_{\pi(\mathrm{asym})}$)	11.5 (φ_{π_1})
I(exp.), eV (Ref.191)	8.0	9.3	11.3

This shows that five 2*p* electrons of the carbon atoms and one 3*p* electron of the silicon atom in the molecule of this compound are delocalised, in full agreement with the characteristics of the formation of aromatic systems. An analogous situation has been observed also in the case of silatoluene[193]. Two ionisation bands in its PES have been assigned: at 7.7 eV to the $\varphi_{\pi(\mathrm{sym})}$ orbital and at 9.15 eV to the $\varphi_{\pi(\mathrm{asym})}$ orbital.

In conformity with the considerably higher energies of the highest occupied molecular orbitals of silabenzene and silatoluene compared with their carbon analogues, the ultraviolet spectra of these compounds exhibit a distinct bathochromic shift of all the absorption bands. As in the ultraviolet spectrum of benzene, three absorption bands are observed in that of silabenzene (at 10 K in an argon matrix): at 212 nm (instead of 180 nm in the benzene spectrum), at 272 nm (instead of 203 nm), and at 315—320 nm (instead of 255—265 nm). The long-wavelength absorption in the ultraviolet spectrum of silatoluene is observed at 315 nm instead of 255—265 nm in the ultraviolet spectrum of toluene[192].

The first compounds with an sp^2-hybridised germanium atom, namely 4-ethyl, and 4-(t-butyl)germatoluenes, have also been synthesised by the pyrolysis of the corresponding cyclohexadienes and investigated by the PES method[194].

Silabenzene and silatoluene proved to be the first compounds with an sp^2-hybridised silicon atom which was sufficiently stable for their study by the PES method. The first communications concerning the synthesis of stable disilenes—compounds with a double bond between two silicon atoms—appeared in 1981—1982.[195-197] For example, tetramesityldisilene[196] $(Me_3C_6H_2)_2Si{=}Si(C_6H_2Me_3)_2$ was obtained by the photolysis of 2,2-dimesitylhexamethyltrisilane[196], while the photolysis of hexakis(2,6-dimethylphenyl)cyclotrisilane yielded the disilene $(Me_2C_6H_3)_2Si{=}Si(C_6H_3Me_2)_2$.[197] It has been shown by X-ray diffraction that the bond length between the silicon atoms in the first of these disilenes is shorter than a single silicon—silicon bond in polysilanes by 10% and its ultraviolet spectrum showed an absorption at a longer wavelength, namely at 272 nm (3.85), 340 nm (3.44), and 422 nm (3.8), compared with the ethylene analogue.

5. The Atoms of the Boron Subgroup Elements

Organic compounds of the boron subgroup elements are distinguished by a high reactivity: they readily oxidise in air, react with electron donors, and tend to polymerise. The corresponding boron compounds are somewhat less reactive. Their PES and their orbital structure have been investigated in greater detail.

The BC_3 fragment in the trimethylborane molecule is planar and the boron atom has orbitals assuming trigonal directions. The first band in the PES of this compound refers to the ionisation of the σ(B—C) orbital and is observed at 10.7 eV; the ionisation of the σ(C—H) orbital is observed at 12.8—14.5 eV.[198]

In the study of the PES of boranes in which the boron atom is linked to unsaturated fragments, attention was concentrated on the estimation of the role of the unoccupied 2*p* orbitals of the boron atom in the formation of the occupied molecular orbitals. Since the boron atom has unoccupied *p* orbitals with the same principal quantum number $n = 2$ as the carbon atom, its corresponding compounds constitute a convenient model for the estimation of the role of the unoccupied orbitals in bonding, particularly in view of the ambiguity of the conclusions concerning the role of the unoccupied *d* orbitals in compounds of the elements in the Third and higher Periods[13-16].

The first attempt to estimate the involvement of the unoccupied *p* orbitals of boron in the interaction with the π orbitals of carbon was undertaken in connection with the comparison of the PES of trivinyl- and triethyl-boranes[199]. The first ionisation potentials of these compounds proved to be virtually identical, namely 9.7 and 9.6 eV respectively, and the ionisation of the π electrons in trivinylborane begins at 10.7 eV, as in ethylene. According to the authors[199], no appreciable mixing of the unoccupied 2*p*(B) orbitals with the π orbitals of the vinyl groups is observed in trivinylborane either as a consequence of the displacement of the orbitals from the plane (with conservation of the sp^2-hybridisation of the boron atom) or owing to the pyramidal structure of trivinylborane.

The involvement of the unoccupied 2*p* orbitals of the boron atom in the formation of the molecular orbitals of phenylboranes has been estimated by Ramsey and O'Neil[200]. As in the case of, for example, phenylsilanes $PhSiX_3$,[179] where the *d* orbitals play a significant role in the formation of the molecular orbitals, a dependence of the contribution of the unoccupied 2*p*(B) orbitals to the molecular π orbitals of the phenylboranes $PhBX_3$ on the character of the substituents X is observed. Fig.2 compares the energies of the π orbitals of various phenylboranes of the type $PhBX_2$. For example, in the PES of $PhBR_2$ the first ionisation potential refers to the ionisation of the a_2 orbital, whose energy increases as a consequence of the electron-donating influence of the group BR_2. It has been found from the results of a

quantum-chemical calculation that the contribution of the $2p$(B) orbital to the $\pi(b_1)$ orbital is considerable and the energy of the molecular orbital is therefore reduced.

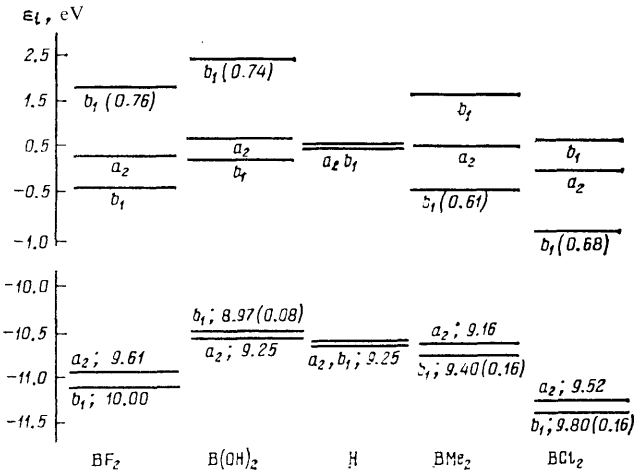


Figure 2. The influence of the substituents BX_2 on the energies of the π orbitals of the phenylboranes $C_6H_5BX_2$ according to PES data (the ionisation potentials are indicated in electron-volts) and CNDO/2 calculations [the energies of the molecular orbitals are indicated along the ordinate and the coefficients of the $2p$(B) orbitals in the corresponding molecular orbitals are indicated in brackets][200].

It was established in the same study[200] that the $2p$(B) orbital makes a considerable contribution to the occupied π orbitals also in dichlorophenylborane. As a consequence of the π-donor influence of the oxygen and fluorine atoms, the degree of involvement of the $2p$(B) orbital in the occupied $\pi(b_1)$ orbitals in the compounds with X=OR and F is reduced but becomes considerable in the unoccupied $\pi^*(b_1)$ orbitals.

6. The Atoms of the Zinc Subgroup Elements

Compounds in which the metal atom is bound to organic groups are known for virtually all the Group II metals. The reactivity of the organic compounds of the beryllium subgroup metals is, however, appreciably higher as a result of which their structure has been scarcely investigated by the PES method. On the other hand, although the zinc subgroup metal atoms have appreciably lower electronegativities than carbon, their organic, including aromatic, compounds are much less reactive; they have found wide applications in organometallic synthesis and are classical objects in theoretical chemistry[201,202]. The mixing of the orbitals in these compounds, in the first place in mercury compounds, has been studied in fair detail.

The C—E—C angles in dialkyl derivatives of Group IIB metals are ~ 180°[78] and the carbon–metal σ-bonds have low ionisation potentials[203–208]; the ionisation potentials of dimethylmercury, for example, are 9.3 and 11.6 eV[203,208]. Both properties specified above promote the mixing of the atomic orbitals of Group IIB metals with the carbon π orbitals in the corresponding organometallic compounds.

The role of the interaction of the σ and π orbitals in the benzyl and allyl compounds of mercury containing the



fragment was first noted by Nesmeyanov as early as 1948[209]; a molecular-orbital interpretation of the effect of the $\sigma-\pi$ conjugation was first achieved in a study of the absorption spectra of charge-transfer complexes[210]; quantitative estimates of the degree of mixing of the σ(C—Hg) and π orbitals in allyl and benzyl compounds of mercury were achieved only when PES was employed[211–218].

In particular, in a study of the PES of allylmercury chloride, Schmidt et al.[211] estimated the degree of mixing of the σ(C—Hg) and carbon π orbitals with the aid of the quantity δE determined from the formula

$$\delta E = (H_{\sigma\pi})^2/\Delta E ,$$

in which ΔE is the difference between the energies of the fragment orbitals and $H_{\sigma\pi}$ the resonance integral for the σ and π orbitals. The values of $H_{\sigma\pi}$ calculated from the PES data for allylmercury chloride and benzylmercury chloride proved to be virtually identical (0.98 and 0.99 eV respectively) and close to the corresponding values for the allyl and benzyl compounds of other metals[212].

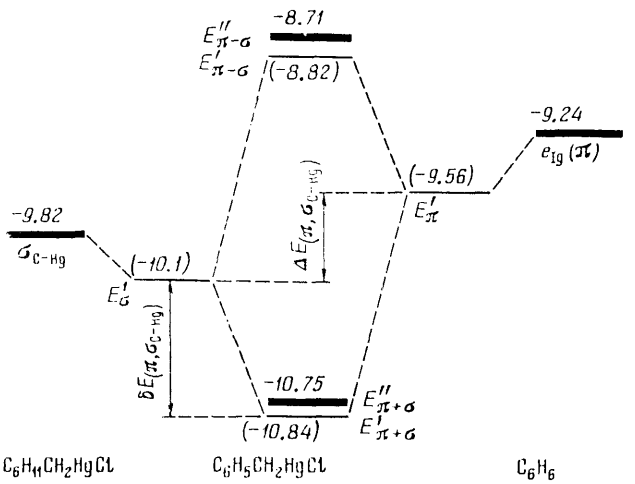


Figure 3. Schematic illustration of the formation of the molecular orbitals of benzylmercury chloride[213] (the energies are indicated in electron-volts).

An attempt has been made[213] to separate the contributions to the molecular orbital energy due to the σ(C—Hg)—π mixing, the inductive effect, and the mixing of the σ(C—Hg) and π orbitals with the σ(C—H) orbitals. Fig. 3 presents a qualitative diagram for the formation of the molecular orbitals of benzylmercury chloride. The value of E(C—Hg) shown in this diagram was found from the correlation between the ionisation potentials of the n(Cl) and σ(C—Hg) orbitals established on the basis of data referring solely to alkylmercury chlorides; the values of E'_{σ}(C—Hg) and E'_{π} were estimated taking into account the inductive effects of the Ph and CH_2HgCl groups respectively; the energies $E'_{\sigma-\pi}$ and $E'_{\sigma+\pi}$ were found from equations proposed[37] for a quantitative description of the $\sigma-\pi$ mixing; the energies $E''_{\sigma-\pi}$ and

$E''_{\sigma+\pi}$ were estimated with the aid of the corresponding ionisation potentials found from the PES of benzylmercury chloride. The difference between the values of $E'_{\sigma-\pi}$ and E'_{π} is equal to the absolute change in the energy of the benzene $b_1(\pi)$ orbital arising owing to its mixing with the σ(C—Hg) orbital and the value 0.74 eV was adopted for it. The differences between the $E''_{\sigma-\pi}$ and $E'_{\sigma-\pi}$ energy levels and also between $E''_{\sigma+\pi}$ and $E'_{\sigma+\pi}$ are associated with the additional destabilisation of the molecular orbitals on mixing of the initial σ(C—Hg) and π orbitals with σ(C—H) orbitals.

It is of interest to compare the values of the integral $H_{\sigma(C-H)\pi}$, characterising the degree of mixing of the σ(C—Hg) and π orbitals, obtained in two ways. One value was found from the data in the diagram (Fig.3):

$$H_{\sigma(C-Hg)\pi} = \sqrt{(-9.56+8.82)(-10.1+8.82)} = -1.0 \text{ eV}.$$

The other, amounting to −1.1 eV, was found from the scheme discussed in the Introduction, i.e. without including the additional effects noted in the diagram but with an appropriate selection of model compounds for the estimation of the energies of the fragment orbitals: the energy of the π orbital was estimated with the aid of the first ionisation potential of benzene, while the first ionisation potential of methylmercury chloride was used to estimate the energy of the σ(C—Hg) orbital[214]:

$$H_{\sigma(C-Hg)\pi} = \sqrt{(-9.24+8.71)(-10.8+8.71)} = -1.1 \text{ eV}.$$

Without overestimating the similarity of the above two estimates of the integral $H_{\sigma(C-H)\pi}$, we emphasise yet again that, with an apt selection of "model" compounds, it is as a rule possible not only to parametrise reliably the quantum-chemical calculations for the corresponding complex compounds on the basis of the PES of the "model" compounds[108] but also one can estimate fairly reliably the degree of mixing of particular atomic or fragment orbitals.

There are few data for the orbital interactions in compounds where the mercury atom is linked directly to carbon π-electron systems[213,218,219]. The ionisation potentials (eV) of phenylmercury chloride PhHgCl [9.40 ($b_1 + a_2$); 10.45 (σ_{C-Hg}); 10.84 (p_{Cl})] and phenylmercury bromide PhHgBr [9.33 ($b_1 + a_2$)] show that the occupied 5*d* and unoccupied 6*p* atomic orbitals of mercury are not effectively mixed with the benzene π orbitals. The same conclusion is valid also for diphenylmercury[219]. On the other hand, the mixing of the $e_{1g}-\pi$ orbitals of propynyl groups and the $e_{1g}(5d_{xz}$ and $5d_{yz})$ orbitals of mercury in mercurialkynes has been observed.

The PES method and the quantum-chemical calculations in the π-approximation parametrised on its basis make it possible to estimate quantitatively the degree of mixing of the orbitals of various elements with the carbon π orbitals in the corresponding organoelemental aromatic compounds. The estimates obtained show that the main factor determining the effectiveness of the mixing is the principal quantum number of the element, i.e. the number of the Period to which it belongs. The most effective π-type mixing with the π orbitals of carbon is that of the corresponding orbitals of the elements in the Second Period.

Nevertheless the atoms of elements having a principal quantum number greater than two are capable of $(p-p)\pi$ bonding both with carbon atoms and with one another contrary to the "classical double bond rule"[220-222]. The parameters $H_{E\pi(sym)}$ and $H_{(CE)\pi(sym)}$, characterising the mixing of the benzene $\phi_{\pi(sym)}$ orbital with the corresponding orbitals localised at the heteroatoms E, are fairly large, their values being listed below for certain Group IV—VII elements (see also Tables 1—3 and 6):

C	N	O	F
−1.03	−1.21	−1.37	−0.84
Si	P	S	Cl
−0.60	−0.34	−0.84	−0.63
Ge	As	Se	Br
−0.54	0.0	−0.72	−0.62

As shown in the present review, the parameters $H_{E\pi(sym)}$, determined from the analysis of the PES of "model" compounds (substituted benzene derivatives) determine unambiguously in their turn the parameters H_{EC} ($H_{EC} = \sqrt{3}H_{E\pi(sym)}$), which characterise the mixing of the orbitals of the element not with the benzene π orbital but with the $2p_{\pi}$ orbital of the carbon atom and are suitable for the estimation and parametrisation of the mixing of the orbitals also in calculations carried out in terms of an atomic basis set. The parameters H_{EC} have been used successfully in the analysis of the molecular orbital structure, particularly in the case of cyclic compounds where the atoms of the elements are present as part of the composition of rings and not as substituents[108-110,129].

The matrix elements $H_{\mu\mu}$ and $H_{\mu\nu}$, used in quantum-chemical calculations by the simple method, have a complex nature: they include also effects determined by the skeletal integrals and the effects of the interelectronic interactions. At the same time it is evident that the diagonal elements $H_{\mu\mu}$ and $H_{\nu\nu}$ depend mainly on the energy of the electron in the μth and νth fragment orbitals respectively, while the non-diagonal elements $H_{\mu\nu}$ depend mainly on the energy of the electron in the region of the mixing of the μth and νth fragment orbitals and thus characterise the degree of their interaction. The parameters $H_{\mu\nu}$, which have a perfectly definite quantum-chemical significance, can, in our view, provide a better understanding of the experimental results in many instances than the numerous constants estimating the conjugation effects. The molecular-orbital characteristics calculated on their basis have been used successfully in the interpretation of the spectra (in the first place photoelectron spectra) and reactivities of complex organoelemental aromatic compounds, including polycyclic compounds.

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Mendeleev Moscow Institute of
Chemical Engineering

Translated from *Uspekhi Khimii*, 53, 925-947 (1984) U.D.C. 546.262.3-31 : 546.264-31 : 542.941 : 542.971.2

Transition Metal Complexes as Catalysts of the Synthesis of Hydrocarbons from Carbon Oxides and Hydrogen

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

The results of studies on the synthesis of hydrocarbons from carbon oxides and hydrogen in the presence of metal complex catalysts are considered and the characteristic features of the activation of CO and CO_2 by transition metal complexes and the mechanisms of the reduction of carbon oxides by hydrogen are discussed.
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I. INTRODUCTION

The synthesis of hydrocarbons from carbon oxides and hydrogen has currently acquired renewed great practical importance as a method for the preparation of motor fuels and valuable chemical products based on coal[1-3]. The inadequate yield of the existing synthetic processes, the lack of catalysts for the specific synthesis of individual hydrocarbons and their narrow fractions, the considerable energy consumption, and also certain technological difficulties due to the need to remove considerable amounts of heat as a consequence of the highly exothermic nature of the reactions must be included among their deficiencies[4]. Both in our country and abroad, a vigorous search is being prosecuted for metal complex catalysts of the synthetic reactions, possessing high activity and selectivity under mild conditions[4,5].

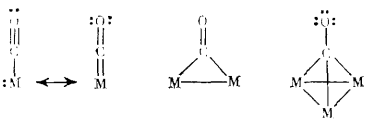
The synthesis of hydrocarbons from carbon oxides and hydrogen in the presence of metal complex catalysts is a comparatively new branch of metal complex catalysis. The first studies in this field were published as late as 1976. The number of publications having a direct bearing on the synthesis of hydrocarbons from CO and H_2 in the presence of transition metal complexes is small —it does not exceed several tens of communications dealing with the modelling of individual stages of the process and proposing reaction mechanisms. A series of reviews have considered the activation of CO [6,7] and CO_2 [7-9] by transition metal complexes, the reduction of CO [6,7] and CO_2 [7,9] to organic compounds, and the synthesis of hydrocarbons from CO and H_2 in the presence of metal complex catalysts[6,7].

The present review deals with methods for the activation of carbon monoxide and with its reactions in the presence of transition metal complexes, including the synthesis of hydrocarbons from CO and H_2; it also discusses the problem of the activation of CO_2 by transition metal complexes. The activation of hydrogen by transition metal complexes has been considered in a monograph[10].

II. THE REDUCTION OF CARBON MONOXIDE IN THE PRESENCE OF TRANSITION METAL COMPLEXES

1. The Ways in which Carbon Monoxide is Coordination to Transition Metals

Examination of various ways in which the CO molecule is coordinated to transition metals makes it possible to infer the degree of activation of the carbonyl ligand and hence to outline procedures for the reduction of carbon monoxide to hydrocarbons or other organic compounds. These procedures are represented below[7]:



(Ia) (Ib) (II) (III)

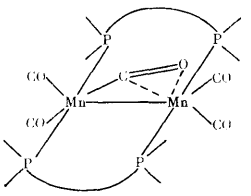
It is well known[11] that in metal carbonyls there is a simultaneous transfer of electrons from the σ orbital of the CO group to the metal atom and from the metal to the π orbital of CO. The transfer of electrons from the *d* orbitals of M to the π orbitals of CO entails a decrease of the C–O bond order and an increase of the metal–carbon bond order; this has been confirmed by infrared spectroscopic data. The stretching vibration frequency in free carbon monoxide is in the range 2146–2170 cm^{-1} and the corresponding vibration frequencies of the terminal CO group of metal carbonyls [structure (I)] have lower values (2000–2100 cm^{-1}).[11] With some approximation, the decrease of the stretching vibration frequency reflects the decrease of the C–O bond force constant and also the bond order. The increase of electron density at the transition metal atoms leads to an increase of the reverse supply of electrons to the π orbitals of CO and to a decrease of the C–O bond order. For example, the stretching vibration frequencies of the CO groups in the isoelectronic and isostructural complexes $[Mn(CO)_6]^+$, $Cr(CO)_6$, and $[V(CO)_6]^-$ are 2096, 2000, and 1859 cm^{-1} respectively[12]. Thus the contribution of the resonance structure (Ib) increases in the sequence Mn, Cr, V. However, the decrease of the bond order for the terminal CO groups of metal carbonyls is insignificant and an appreciable charge in the C–O bond length has not been observed[13].

The stretching vibration frequencies of the bridging carbonyl groups [structure (II)] are in the range 1700–1850 cm^{-1} and the C–O bond order is two and in some cases even less. Despite the outward analogy of the bridging carbonyl groups and organic carbonyl compounds (ketones, aldehydes, etc.), the character of the C–O bond in these compounds differs appreciably. Firstly, the transition metal atom is less electronegative than the carbon atom, which leads to a greater polarisation of the M–C bond compared with the C–C bond. Secondly, the MCM angle is much smaller than that at carbon in the sp^2-hybridised state and amounts to, for example, 83° for $Co_2(CO)_8$ and 77° for $Fe_2(CO)_9$.[14,15] Furthermore, the metal–metal bond shields the carbon atom of the bridging carbonyl ligand. For the reasons indicated above, the bridging carbonyl group is less reactive with

respect to nucleophilic attack on the carbon atom than the carbonyl groups in organic compounds.

The bridging carbonyl groups bound to three metal atoms [structure (III)] are inadequately described by the valence bond method. However, it is evident that an appreciable decrease of the C–O bond order is attained in this case because the stretching vibration frequencies in μ^3-CO are in the region of 1600 cm^{-1}. At the same time the bridging carbonyl groups bounds to three metal atoms are characterised by longer C–O bonds. For example, the C–O distance in $Rh_6(CO)_{16}$ is 1.155 ± 0.015 Å for the terminal groups and 1.201 ± 0.022 Å for the bridging groups[16].

Thus, depending on the nature of the complex and on the mode of coordination of the carbonyl ligand, the latter exhibits different reactivities, which are determined by the redistribution of electron density in the M_nCO system. An extremely unusual mode of coordination of the CO group has been observed comparatively recently. The complex $Mn_2(CO)_5(dppe)_2$, where dppe = bis(diphenylphosphino)-ethane[17], coordinates the CO molecule in accordance with the scheme below:

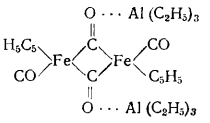


In this case the carbonyl ligand forms a σ-bond with one Mn atom and a π-bond with the other, which leads to an unexpectedly low stretching vibration frequency of CO (1645 cm^{-1}).

2. The Reactivity of the Carbonyl Ligand

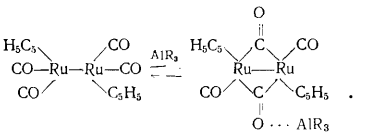
When a CO molecule is coordinated to two or more transition metal atoms, as indicated above, the C–O bond order is appreciably reduced. Thus the bridging carbonyl groups are activated to a greater extent by the transition metal than the terminal groups[18]. This type of coordination of CO obtains in carbonyl clusters and has much in common with the dissociative adsorption of CO on metal surfaces, including metals forming part of the composition of heterogeneous catalysts. Presumably the bridging carbonyl ligands bound to three carbon atoms are activated to the greatest extent. However, convincing evidence confirming their enhanced reactivity has not so far been obtained.

An appreciable increase of the reactivity of the carbon ligand is achieved when it interacts with Lewis acids[19,20]. Such interaction is characteristic of the strongest Lewis acids—derivatives of boron and aluminium. The possibility of adding a Lewis acid to the oxygen atom of the carbony ligand was observed for the first time by Schriver and co-workers[21,22] for the bridging CO groups in the complex $[(C_5H_5)Fe(CO)_2]_2$, which forms an adduct with two $Al(C_2H_5)_3$ molecules:



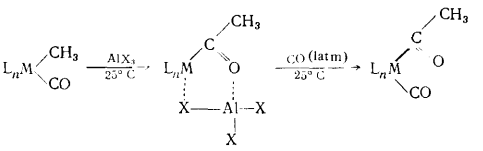
The structure of the adduct was established by X-ray diffraction[21]. Its formation reduces greatly the stretching vibration frequencies of the bridging CO groups involved in the interaction with the Al atom and some increase of the stretching vibration frequencies of the terminal carbonyl ligand. The decrease of the stretching vibration frequencies of the CO groups bound to Al is induced by the weakening of the C–O bonds as a consequence of the shift of electron density towards the electron acceptor molecule, which entails a decreased electron density at the transition metal atom and hence increased stretching vibration frequencies of the terminal CO groups.

The study of the interactions of complexes containing both bridging and terminal CO groups with Lewis acids has shown that the bridging CO groups are more basic. The basicity of the oxygen atom of the CO group increases in the sequence terminal groups < doubly bridging groups < triply bridging groups[19]. The differences between the basicities can be used to shift the equilibrium and to convert terminal groups into bridging groups; for example[23]:



Thus the action of the Lewis acid alters the structural parameters of the carbonyl ligand and leads to a redistribution of electron density, which favours nucleophilic attack on the carbon atom of the coordinated CO molecule.

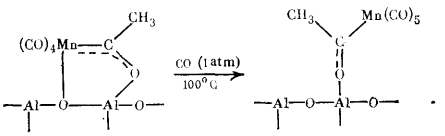
It has been shown[24,25] that the Lewis acids BX_3 (X = F, Cl, or Br) and AlX_3 (X = Cl, Br, CH_3, or iso-C_4H_9) catalyse the insertion of CO into the M–C bond:



$L_nM(CH_3)(CO)$ = $(CO)_5MnCH_3$, $(CO)_5MoCH_3$, $(C_5H_5)(CO)_3MoCH_3$ and $(C_5H_5)(CO)_2FeCH_3$.

The rate of insertion of CO increases by several orders of magnitude under these conditions. In certain cases, this reaction does not occur in the absence of the Lewis acid at a CO pressure of 1 atm and 25 °C. For example, the insertion of CO in the Fe–C bond of $(C_5H_5)(CO)_2FeCH_3$ occurs only at a CO pressure of 136 atm and 125 °C in the absence of AlX_3. The structure of the intermediate acyl complexes bound to the Lewis acid was established by X-ray diffraction[25].

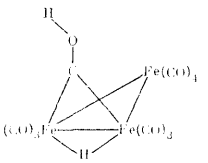
It is of very great interest that the above reaction is catalysed also by Al_2O_3.[26] It was found that, when $(CO)_5MnCH_3$ is deposited from pentane onto an Al_2O_3 film which had been heated to 500° or 1000 °C, the CO is inserted to the Mn–C bond at 25 °C. On the basis of the analysis of the infrared spectra, the authors[26] propose the following structure of the adducts:



In contrast to the adducts with molecular Lewis acids (AlX_3 and BX_3), in this case the successive addition of CO molecules takes place at higher temperatures (100 °C).

Thus the data presented above permit the conclusion that the Lewis acid significantly activates the carbonyl ligand in relation to nucleophilic attack on the carbon atom. The insertion of CO in the Mn–C bond on the Al_2O_3 surface is of fundamental importance because it is directly related to the mechanisms of the Fischer–Tropsch reaction in the presence of heterogeneous catalysts.

Reports of the activation of the carbonyl ligand by protic acids have appeared recently. It has been shown[27] that treatment of $[HFe_3(CO)_{11}]^-$ with a solution of HSO_3F in anhydrous CD_2Cl_2 leads to the formation of the compound $H_2Fe_3(CO)_{11}$, which has an extremely unusual structure according to ^1H NMR data and contains a protonated carbonyl ligand:



The same group of investigators were then able to show[28,29] that the carbonyl ligand activated in this way is capable of being reduced to CH_4 under mild conditions:

$$[Fe_3(CO)_{13}]^{2-} + HSO_3CF_3 \xrightarrow{25^\circ C} CH_4 + H_2 + CO + Fe^{2+} + SO_3CF_3^- .$$

The yield of CH_4 was 0.56 mole per mole of the cluster in three days. The presence of even trace amounts of water greatly reduced the rate of reaction.

3. The Reduction of the Carbonyl Ligand

The possibility of reducing the carbonyl ligand to the formyl ligand was first demonstrated in 1976.[30] It was found that, when various carbonyl complexes in tetrahydrofuran (THF) are treated with $Na[HB(OCH_3)_3]$ at 25 °C, the formyl derivatives are formed:

$$M(CO)_n + [HB(OCH_3)_3]^- \rightarrow \left[(CO)_{n-1}M-C\begin{matrix}O\\H\end{matrix}\right]^- + B(OCH_3)_3 .$$

The formation of the formyl ligand was detected by ^1H NMR, ^{13}C NMR, and infrared spectroscopic methods. On reduction of $Fe(CO)_5$, the formyl ligand was activated in the form of $[(Ph_3P)_2N][(CO)_4FeCHO]$ in 39% yield. A series of communications[31–44] on the synthesis of formyl complexes were published in subsequent years. It was shown[31,32] that the reduction of $[(C_5H_5)Re(CO)_2(NO)]BF_4$ with $Li[HB(C_2H_5)_3]$ in THF at 0–25 °C leads to the formation of mono- and di-formyl complexes, while BH_3 reduces the formyl ligand to the methyl ligand under the same conditions:

$$[(C_5H_5)Re(CO)_2NO]^+ \xrightarrow{HB(C_2H_5)_3^-} (C_5H_5)Re(CO)(NO)(CHO) \rightarrow \begin{cases} \xrightarrow{BH_3\cdot THF} (C_5H_5)Re(CO)(NO)(CH_3) \\ \xrightarrow{HB(C_2H_5)_3^-} (C_5H_5)Re(NO)(CHO)_2 \end{cases} .$$

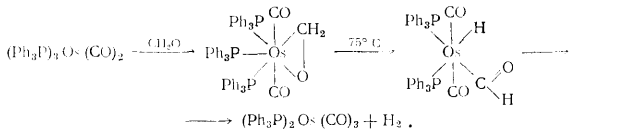
Another groups of investigators[33,34] were able to demonstrate the formation of the hydroxymethyl complex on reduction of the carbonyl ligand with $NaBH_4$ in THF at 0–25 °C:

$$[(C_5H_5)Re(CO)_2NO]^+ \xrightarrow{NaBH_4} (C_5H_5)Re(CO)(NO)X ;$$
$$X = CHO, CH_2OH, CH_3 .$$

Depending on the reaction conditions, it is possible to isolate formyl, hydroxymethyl, or methyl complexes.

Treatment of $Os_3(CO)_{12}$ or $Ir_4(CO)_{12}$ with $Li[HB(C_2H_5)_3]$ leads to the reduction of one of the carbonyl ligands to the formyl ligand[35,36] and the formation of the cluster anions $[Os_3(CO)_{11}(CHO)]^-$ or $[Ir_4(CO)_{11}(CHO)]^-$. The latter anion decomposes with formation of the hydride complex $[Ir_4(CO)_{11}H]^-$.

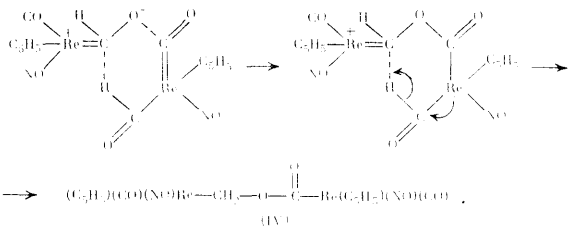
An osmium complex[27] containing coordinated formaldehyde, which is a tautomer of the hydroxymethylene ligand $-C\begin{matrix}H\\OH\end{matrix}$ has been synthesised:[37]



On heating, the complex decomposes with evolution of H_2 and formation of $(Ph_3P)_2Os(CO)_3$.

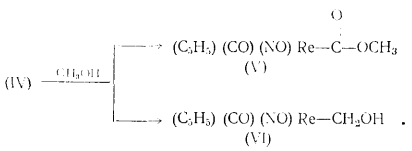
Studies have shown[38–40] that the formyl complexes behave as donors of the hydride ion. For example, when $[(C_2H_5)_4N]\cdot[(PhO)_3PFe(CO)_3(CHO)]$ reacts with $Re_2(CO)_{10}$, a formyl complex of rhenium is formed: in the case of acetone, isopropyl alcohol is produced and in the case of alkyl halides, the products are alkanes.

A hydride ion need not be transferred only to another transition metal complex. The disproportionation of formyl complexes with transfer of a hydride ion to the formyl ligand in accordance with the following scheme has been described[41,42]:



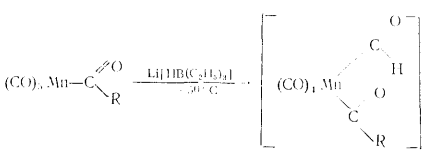
(IV)

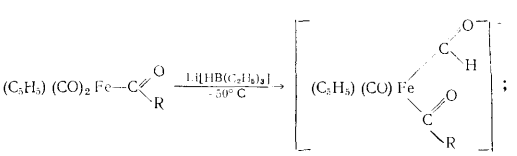
The metalloester (IV) has been isolated and characterised by ^1H NMR and infrared spectroscopy. Its methanolysis leads to the formation of the methyl ester of the metalcarboxylic acid (V) and to the hydroxymethyl complex (VI):



Dinuclear formyl complexes[43] of the type $Li[(CO)_5MM'(CO)_4\cdot(CHO)]$, where M = M' = Re or M = Re and M' = Mn, were first obtained from $Li[HB(C_2H_5)_3]$ and $ReMn(CO)_{10}$ or $Re_2(CO)_{10}$ at 25 °C.[43] Treatment of these complexes with an excess of $K[HB(t\text{-}C_4H_9)_3]$ leads to the formation of formaldehyde and methanol in yields of 21 and 38% respectively.

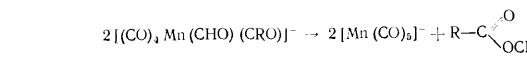
Formyl complexes of Mn and Fe containing an acyl ligand have been recently synthesised and characterised[45]:





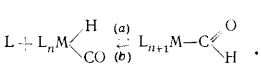
R = Ph, CH_2OCH_3, $COOCH_3$, CF_3, CH_3 .

These complexes decompose at room temperature in accordance with the scheme



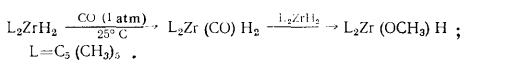
It has been suggested that the decomposition of these complexes entails a transfer of the hydride ion from the formyl to the acyl ligand[45].

Thus it has now been reliably demonstrated that formyl complexes of transition metals exist. It has been established that the reduction of the carbonyl ligand by an active donor of the hydride ion leads to the formyl ligand and in certain cases the latter is reduced with formation of the hydroxymethyl or methyl groups. The study of the properties of the formyl complexes showed that they are capable of transferring the hydride ion to the carbonyl[38–40], formyl[41,42], or acyl[45] ligand and also to ketones and alkyl halides[38–40]. It is noteworthy that in the cases indicated above it is suggested that the formyl ligand is formed on treatment with a hydride ion donor, namely BH_3, $NaBH_4$, $Li[HB(C_2H_5)_3]$, etc., i.e. as a result of the nucleophilic attack by the hydride ion on the carbonyl ligand. There has been only one communication[46] on the synthesis of a formyl complex as a result of the insertion of the CO group in the Rh–H bond [reaction (*a*)]. Furthermore, all the formyl complexes synthesised hitherto are coordination-saturated and reaction (b) is therefore hindered, although at elevated temperatures the ligand is split off and a carbonyl hydride complex is formed[35]:

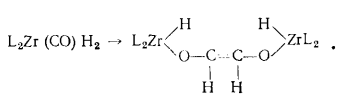


On the other hand, there exist many instances of the insertion of CO in a transition metal–carbon bond with formation of acyl complexes[47]. The formation of formyl complexes from hydrocarbonyls is thermodynamically less favourable than the formation of acyl complexes from alkyl carbonyls.

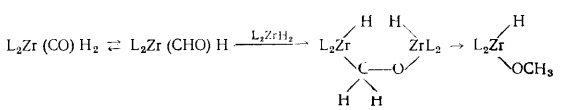
In 1976 the reduction of the carbonyl ligand to the methoxy-group was reported[48]:



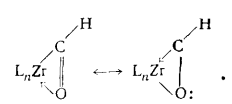
Hydrolysis of the resulting complex leads to the formation of methanol. In the absence of an excess of L_2ZrH_3, the carbonyl hydride complex $L_2Zr(CO)H_2$ dimerises according to the scheme



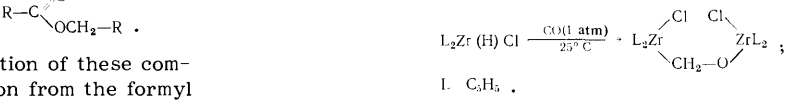
The authors[48] proposed a reaction mechanism with the intermediate formation of a formyl complex:



Subsequent investigations of this reaction led the authors[49] to the conclusion that the formyl complex formed on insertion of CO in the Zr–H bond can be stabilised as a consequence of the formation of a π-bond, as in the stabilisation of an acyl ligand[50]:

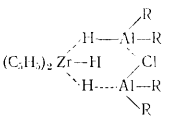


When CO interacts with zirconium halide hydride, a dinuclear complex is also formed and hydrolyses with formation of CH_3OH: [51]



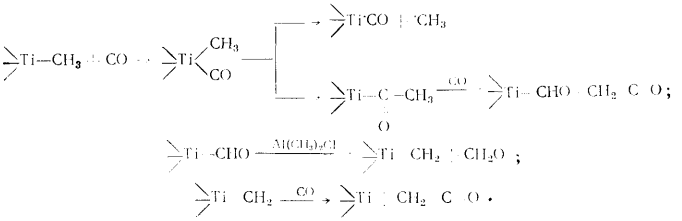
Thus zirconium hydride complexes reduce carbon monoxide under mild conditions. In this case the formation of the coordination-unsaturated formyl complex $L_2Zr(CHO)H$ as a result of the insertion of CO in the Zr–H bond has been postulated. The complex is stabilised by the additional π-binding of the formyl ligand.

In the presence of $HAlR_2$ (R = iso-C_4H_9) and $(C_5H_5)ZrCl_2$, it has been possible to reduce CO to linear alcohols[52]. The reaction proceeds at 25 °C and a carbon monoxide pressure of 1–4 atm in benzene. The formation of a zirconium hydride complex during the course of the reaction has been postulated:



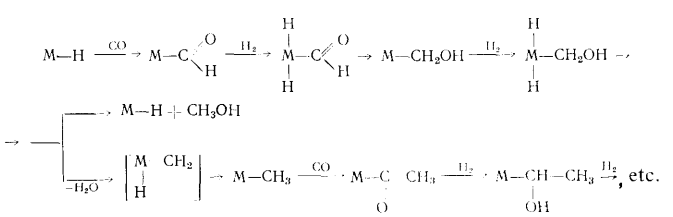
As a result of the interaction of this complex with CO and subsequent hydrolysis, a mixture of normal alcohols in the molar proportions $C_1 : C_2 : C_3 : C_4 = 1 : 0.12 : 0.15 : 0.03$ is formed. An excess of $HAlR_2$ inhibits the reaction but up to ten $HAlR_2$ addition cycles can be carried out without an appreciable decrease of activity. The use of ^{13}CO leads to the formation of $^{13}CH_3OH$.

Enikolopyan and co-workers observed that, in the presence of $Al(CH_3)_2Cl$, $(C_5H_5)_2TiCl_2$ catalyses the reduction of CO at 20–50 °C and atmospheric pressure to formaldehyde and keten. The introduction of $LiAlH_4$ into this catalytic system increases its activity (three moles of CH_2O per gramme-atom of Ti are formed in 1 h at 50 °C under 1 atm CO pressure). The authors[53] suggested the following reaction mechanism:



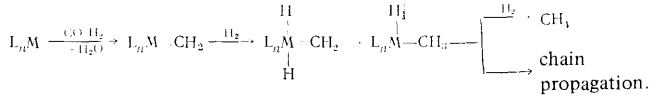
The study of model reactions involving the reduction of the carbonyl ligand and also the formation of complexes containing the formyl, hydroxymethyl, and methyl ligands on reduction of the coordinated CO molecule suggested a number of mechanisms of the CO hydrogenation reaction catalysed by transition metal complexes.

The following mechanism has been proposed for the process[54]:

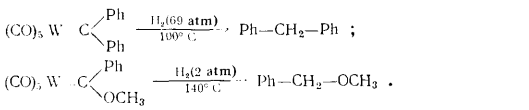


The authors were unable to confirm it experimentally because most of the studies on the CO reduction reaction were published subsequently.

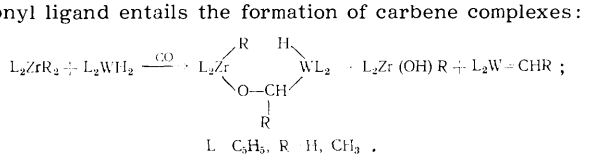
In 1976 it was suggested[30] that the reduction of the carbonyl ligand should lead to the formation of a carbene complex:



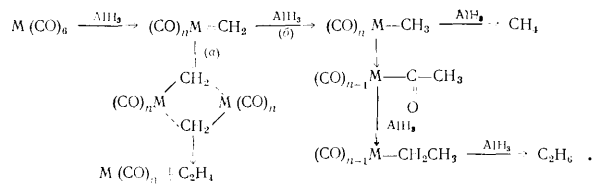
It has been shown that the carbene complexes are reduced with formation of alkanes:



Subsequent studies[55,56] confirmed that the reduction of the carbonyl ligand entails the formation of carbene complexes:

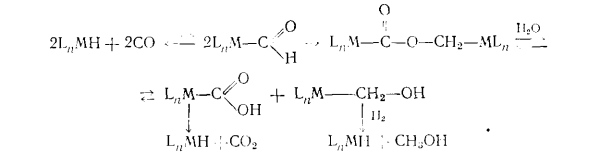


Treatment of $Ru_3(CO)_{12}$, $Cr(CO)_6$, $Mo(CO)_6$, or $W(CO)_6$ with aluminium hydride in THF at 22 °C leads to a rapid evolution of C_1–C_3 hydrocarbons[57]. The ethylene content in the reaction product is 95% for chromium, molybdenum, and tungsten carbonyls. Not more than two carbonyl groups of the complex are reduced during the reaction and the solution remains homogeneous. The activity of $LiAlH_4$ is somewhat lower if BH_3 is inactive. A mechanism involving the formation of a carbene complex has been postulated[57]:



The selective formation of C_2H_4 has been explained by the preferential occurrence of the process via pathway (*a*). It may be that the carbonyl ligand is activated as a result of the binary coordination of the CO group: M–CO...AlH_3.

A mechanism for the reduction of CO involving a stage in which formyl complexes disproportionate has also been proposed[41]:

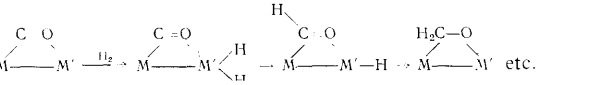


The authors observed[58] that the decomposition of the carbonyls $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Os_6(CO)_{16}$, $Rh_4(CO)_{12}$, and $Ir_4(CO)_{12}$ on the surfaces of Al_2O_3, SiO_2, or MgO at 250° to 400 °C in argon leads to the formation of C_1–C_3 alkanes and CO_2. The selectivity in the formation of CH_4 is 59–100%, depending on the nature of the complex. When the reaction is carried out in an atmosphere of CO, 5–13 moles of CH_4 and 40–90 moles of CO_2 are formed per mole of the complex. The authors suggest that the carbonyl ligand initially reacts with H_2O or surface OH groups of the oxide with formation of CO_2, after which the carbonyl ligand is reduced with hydrogen.

A more detailed study of this reaction showed[59] that hydrocarbons are formed from both polynuclear and mononuclear carbonyls and that in the case of the latter [$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and $Fe(CO)_5$] the maximum yield of CH_4 per gramme-atom of the metal is achieved. The authors[59] concluded that the synthesis of hydrocarbons in this instance does not require a catalyst of the cluster type and proposed a mechanism of the formation of methane in which H_2 plays an unusual role:

$$4OH(ads) + M(CO) \rightarrow MO_3 + 2O^-(ads) + CH_4 ;$$
$$3H_2 + MO_3 \rightarrow M + 3H_2O ;$$
$$\underline{2H_2O + 2O^-(ads) \rightarrow 4OH^-(ads)} \quad ;$$
$$CO + H_2 \rightarrow CH_4 + H_2O .$$

Inspection of the mechanisms presented above as well as the mechanisms of the model reactions involving the reduction of the carbonyl ligand permits the conclusion that the process can proceed with participation of a mononuclear complex rather than a cluster. On the other hand, it has been suggested[18,60] that carbon monoxide is reduced most readily in the presence of cluster catalysts because in the latter there is a possibility of the formation of active intermediates of the type M–CO–M', where M and M' are transition metal atoms:



Experimental confirmation of the existence of such structures has not so far been obtained, although they are known for transition metal complexes containing molecules with triple bonds (N_2 and C_2H_2).[60] It is believed[18,60] that the formation of intermediates of the type M–CO–M' and their hydrogenation may be energetically more favourable than the reduction of the CO molecule coordinated to one transition metal atom. Unfortunately both the possibility of the formation of such structures in carbonyl clusters and the possibility of the hydrogenation of CO with their intermediate formation have not so far been rigorously demonstrated[60–62].

We may note that, as stated above, the binary coordination of the carbon monoxide molecule (M–CO...M') is achieved in the adducts of metal carbonyls with Lewis acids. It has also been suggested that dinuclear complexes of the type L_nZr–CO–ZrL_n (L is the ligand) are formed on reduction of the carbonyl ligand to $-OCH_3$.

Thus examination of the above mechanisms of the reduction of CO with participation of transition metal complexes permits the conclusion that the most active catalytic system for the activation of CO is obtained on binary coordination of carbon monoxide of the type M–CO...M' or M–CO–M'.

4. The Synthesis of Hydrocarbons from CO and H_2

In 1976 Muetterties and co-workers[63] demonstrated for the first time that the synthesis of hydrocarbons from CO and H_2 can be catalysed by transition metal complexes. Methane is formed in the presence of $Ir_4(CO)_{12}$ or $Os_3(CO)_{12}$ in toluene at 140 °C and atmospheric pressure of the 1 : 4 CO–H_2 mixture. However, the rate of reaction is low and the degree of conversion of CO amounted to 1% after 3–5 days. The addition of Ph_3P or $(CH_3O)_3P$ increases slightly the activity of the catalyst.

The non-catalytic reduction of the carbonyl ligand occurs in the presence of niobium hydride complexes[64,65]. Treatment of $(C_5H_5)_2Nb(CO)H$ with hydrogen at 140 °C and a pressure of 1 atm in organic solvents leads to the formation of methane[64]. However, only the carbonyl ligand is then

reduced, which was demonstrated using $(C_5H_5)_2Nb(^{13}CO)H$. The introduction of a mixture of CO and H_2 into the system did not increase the yield of CH_4. The hydride complex $(C_5H_5)_2NbH_3$ reduces the carbonyl ligand to $Cr(CO)_6$ at 45 °C in benzene and an H_2 pressure of 1 atm;[65] this involves the formation of CH_4 and C_2H_6 (10% per gramme-atom of niobium). The yield does not increase when CO is introduced into the system and Cr_2O_3 and $(C_5H_5)_2Nb(CO)H$ are formed at the end of the reaction.

Another example of the non-catalytic reduction of CO by hydrogen to CH_4 is the reaction of $(C_5H_5)_2Ti(CO)_2$ with H_2 at 150 °C in toluene[66]. When D_2 is employed, CD_4 is formed. The authors[66] do not present quantitative data for the yield of CH_4, but state that the reaction is non-catalytic and that the introduction of CO into the system does not increase that the introduction of CO into the system does not increase the yield of CH_4. At the end of the reaction, a cluster having the composition $Ti_6O_8(C_5H_5)_6$ was isolated and its structure was determined. Apparently the formation of $Ti_6O_8 \cdot (C_5H_5)_6$ is caused by the interaction of the titanium complex with water formed in the course of the synthesis of CH_4 from CO and H_2.

The most active catalytic system at atmospheric pressure has been proposed by Demitras and Muetterties[67]. It includes iridium, rhodium, or ruthenium carbonyls and the Lewis acids $AlCl_3$, $AlBr_3$, and BBr_3.[67,69] When the reaction is carried out in a Lewis acid melt without solvent with the ratio $CO : H_2 = 1 : 3$ at 180 °C and 1 atm, C_1–C_4 alkanes are formed. The complexes can then be arranged in the following activity series: $Ir_4(CO)_{12} \cong Rh_6(CO)_{16} \cong Rh_4(CO)_{12} > Ru_3(CO)_{12} \gg H_2PtCl_6 > PdCl_2$. The complexes $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, $NiCl_2$, and $Co_4(CO)_{12}$ showed no activity. It is noteworthy that the activity series for the complex catalysts differs significantly from that for deposited heterogeneous catalysts in the methane formation reaction[70]. The catalytic activity of $Ir_4(CO)_{12}$ is such that 5 moles of CO enter into the reaction per mole of the complex in 1 h. During the reaction, the system remains homogeneous and the formation of metallic iridium is not observed. Furthermore, kinetic calculations based on the activity data for heterogeneous iridium catalysts showed that, even if the entire iridium from the initial $Ir_4(CO)_{12}$ catalyst were reduced to the metal and each metal atom functioned as an active centre for the methane formation reaction, then the calculated rate of reaction would have been lower by several orders of magnitude than the observed rate in the $Ir_4(CO)_{12}$–$AlCl_3$ system.[67] The introduction of metallic aluminium into the given catalytic system resulted in a sharp increase of the yield of hydrocarbons under the same conditions[71–73]. An appreciable alteration of the reaction products and an increase of the degree of conversion of CO are then observed[72].

Similarly the introduction of metallic aluminium into the "transition metal complex–$AlBr_3$" system led to a sharp increase of the yield of hydrocarbons when iridium, ruthenium, and particularly osmium and nickel carbonyls were employed under the same conditions[74]. The complex-forming metals used can be arranged in the following series in terms of their activities: Rh > Ir > Ru > Os > Ni (Table 1). This activity series differs from the analogous series for the M_nL_m–$AlCl_3$ systems presented above. The composition of the reaction products depends on the nature of the catalyst; in the presence of $Ir_4(CO)_{12}$ the main product is CH_4, while in the presence of $Rh_4(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$, appreciable amounts of C_4H_{10} and less C_2H_6 and C_3H_8 are formed together with CH_4. The degree of conversion of CO into hydrocarbons during the experiment then reaches 89% or 22 moles of CO per gramme-atom of rhodium. For the most active systems based on rhodium complexes, a study was made of the influence of the structure of the rhodium complex on the properties of the Rh_nL_m–$AlBr_3$–Al system[72] (Table 1). It was found that both mononuclear complexes and clusters exhibit virtually identical activities per gramme-atom of rhodium.

Table 1. The degrees of conversion of carbon monoxide (K_{CO}, mol CO/g-atom M) and the composition of the reaction products (vol.%) in the synthesis of alkanes from CO and H_2 in the presence of transition metal complexes.

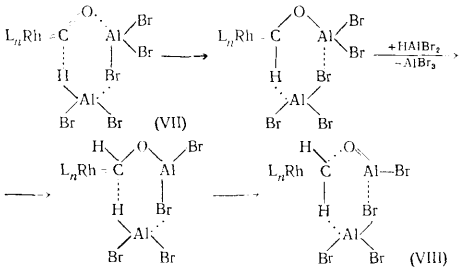
Complex	K_{CO}	CH_4	C_2H_6	C_3H_8	iso-C_4H_{10}	n-C_4H_{10}
$Rh_4(CO)_{12}$	22	47	8	14	30	1
$[Rh(CO)_2Cl]_2$	22	47	8	14	29	2
$Na_3[Rh_{12}(CO)_{30}]$	22	46	9	15	29	1
$(Ph_3P)_3RhCl$	21	50	6	13	30	1
$RhCl_3 \cdot 3H_2O$	3	37	13	12	35	3
$Ir_4(CO)_{12}$	12	73	9	8	9	1
$Ru_3(CO)_{12}$	7	50	5	9	35	1
$Os_3(CO)_{12}$	6	33	11	12	43	1
$NiCl_2$	3	33	16	13	36	2

Note: Conditions: 150°, 10 h, $CO : H_2 = 1 : 4$, molar ratios $M : AlBr_3 : Al : Co = 1 : 200 : 40 : 25$; the following catalysts showed no activity: $Fe(CO)_5$, $Co_2(CO)_8$, $(Ph_3P)_2PdCl_2$, $Mn_2(CO)_{10}$, $Mo(CO)_6$, $W(CO)_6$, and $TiCl_4$.

It was demonstrated by infrared spectroscopy[74] that in the course of the synthesis from CO and H_2 the initial rhodium complexes are converted into a mononuclear anion of the type $[Rh(CO)_2Br_2]^-$. Thus the data presented show that the synthesis of alkanes from CO and H_2 in the presence of the Rh_nL_m–$AlBr_3$–Al catalytic system proceeds on a mononuclear rhodium complex.

The study of the influence of the amount of metallic aluminium in the $Rh_4(CO)_{12}$–$AlBr_3$–Al system[72] showed that an increase of the ratio $Al : AlBr_3$ increases K_{CO} and the C_4H_{10} content in the products of the synthesis; at the same time there is a sharp decrease of the amount of CO_2. The authors[74] suggested the formation of $HAlBr_2$ from H_2, $AlBr_3$, and Al during the synthesis of alkanes from CO and H_2. The presence of $HAlBr_2$ was confirmed by the reduction of acetone to isopropyl alcohol. It was found that, when the $AlBr_3$–Al system was dissolved in THF and treated with a 1 : 4 CO–H_2 mixture at 150 °C, solutions capable of reducing acetone were formed. The reaction with solutions known beforehand to contain $HAlBr_2$, obtained from $LiAlH_4$ and $AlBr_3$, proceeded analogously. In addition, the amount of isopropyl alcohol formed and hence of $HAlBr_2$ was directly proportional to the aluminium content in the $Rh_4(CO)_{12}$–$AlBr_3$–Al system. Thus an increase of the content of aluminium in the $Rh_4(CO)_{12}$–$AlBr_3$–Al system entails an increase of K_{CO} and at the same time also an increase of the amount of $HAlBr_2$ formed during synthesis.

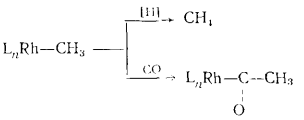
On the basis of the data obtained, the authors[74] proposed the following mechanism of the synthesis of hydrocarbons from CO and H_2 in the presence of the "rhodium complex–$AlBr_3$–Al" catalytic system:



The carbene complex formed and incorporated in the intermediate (VIII) can then be reduced to the methyl complex:

$$L_nRh{=}CH_2 \xrightarrow{[H]} L_nRh{-}CH_3 .$$

On further hydrogenation, this complex gives rise to an alkane or CO is inserted in the Rh–C bond and the resulting acyl complex is reduced in accordance with the mechanism presented above to the ethyl complex of rhodium:

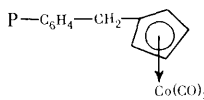


It has been observed[75] that in the presence of the $W(CO)_6$–$AlCl_3$ catalytic system at 200 °C and a pressure of the CO–H_2 mixture of 120 atm, alkylbenzenes are formed from benzene:

$$C_6H_6 + CO + H_2 \rightarrow Ph{-}(CH_2)_n{-}H .$$

The length of the aliphatic chain of alkylbenzenes is consistent with the Schulz–Flory distribution characteristic of heterogeneous catalysts of the Fischer–Tropsch synthesis[76]. The molar ratios of the products were $PhCH_3 : PhC_2H_5 : PhC_3H_7 : PhC_4H_9 : PhC_5H_{11} = 25 : 39 : 1 : 0.1 : 0.1$.[75]

A catalyst containing the cobalt carbonyl complex grafted to a polymer (P) has been proposed for the synthesis of hydrocarbons from CO and H_2:[77]



At 190–200 °C and a pressure of the 1 : 3 CO–H_2 mixture of 30 atm and using n-octane as the solvent, a mixture of C_1–C_{20} hydrocarbons was obtained. The content of hydrocarbons in the products of the synthesis decreases uniformly with increase of their molecular weight. The catalyst exhibits a fairly low activity: 1×10^{-5} mole of CO is consumed per gramme-atom of cobalt in 1 h. The catalytic system containing $Al(C_2H_5)_3$ and the nickel salt of a carboxylic acid with 8–10 carbon atoms, dissolved in a hydrocarbon solvent, proved to be more active[78]. At 330 °C and a pressure of the mixture ($CO : H_2 = 1 : 4$) of 8 atm, the formation of C_1–C_4 hydrocarbons was observed (91% CH_4, 6% C_2H_6, 2% C_3H_8, and 1% C_4H_{10}). After 8 h, the degree of conversion of CO was 62%; a gaseous mixture containing 31 vol.% of the hydrocarbon was formed.

In the presence of cobalt acetylacetonate and $Al(C_2H_5)_3$ dissolved in alkylterphenyl, the formation of C_1–C_6 hydrocarbons from a 1 : 1 CO–H_2 mixture was observed at 190 °C and 1 atm.[79] The rate of formation of the hydrocarbons was 4.4×10^{-4} mole C/h g CO.

The use of $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Ir_4(CO)_{12}$ as catalysts of the Fischer–Tropsch synthesis in THF or n-heptane as the solvent has been described[80]. At 300 °C and a pressure of the mixture ($CO : H_2 = 1 : 1$) of 200 atm, a mixture of C_1–C_{30} hydrocarbons was obtained after 20 h (1.9 moles of C_{10}–C_{20} and 0.6 mole of C_{20}–C_{30} per mole of the catalyst). However, the study of the kinetics of the reaction and the infrared spectra of the reaction mixture under the conditions of the synthesis showed[81,82] that the true catalyst of the synthesis of hydrocarbons in this case was metallic ruthenium formed from $Ru_3(CO)_{12}$. Apparently reports of the metal complex catalysis of the Fischer–Tropsch reaction at temperatures above 200 °C should be treated with some caution, because the majority of the transition metal complexes are unstable under these conditions.

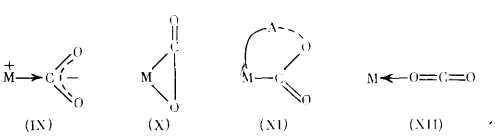
Layer compounds of graphite with transition metals occupy a position intermediate between homogeneous metal complex systems and heterogeneous catalysts of the Fischer–Tropsch reaction. It has been shown that at 300–350 °C the layer compounds of graphite with Group IV–VIII transition metals and potassium catalyse the synthesis of C_1–C_5 hydrocarbons from a mixture of CO and H_2 at 1 atm;[83,84] the main product of the synthesis is CH_4. The activity of layer compounds of graphite with $FeCl_2$ in the synthesis of hydrocarbons from CO and H_2 has been reported recently[85]. This catalyst is active in the synthesis of C_1–C_4 hydrocarbons from CO and H_2 at 300–500 °C and 1–20 atm; the main product of the synthesis is methane (70–90%).

Thus the survey of the literature dealing with the application of metal complex catalysts in the Fischer–Tropsch reaction permits the conclusion that homogeneous systems superior in their activity to traditional heterogeneous catalysts can be developed in principle. This problem has attracted many investigators both in our country and abroad as shown by the constant growth of the number of publications devoted to the application of metal complex catalysts in the reduction of CO to hydrocarbons. The development of studies in this field permits the hope that significant advances will be made in the immediate future.

III. THE REDUCTION OF CARBON DIOXIDE

1. The Ways in which Carbon Dioxide is Coordinated to Transition Metals

The activation of carbon dioxide by transition metals is directly related to the mode of formation of the bond between CO_2 and the transition metal. The coordination chemistry of CO_2 is a comparatively new field of the chemistry of organometallic compounds. The first complex containing the CO_2 molecule was synthesised by Vol'pin and Kolomnikov in 1969.[86] However, to date only a few complexes with CO_2 have been obtained when the structure has been established reliably. In principle the bond between CO_2 and the metal can be formed in accordance with the following schemes[8,9]:



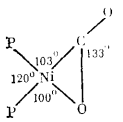
(IX) (X) (XI) (XII)

The interaction of the carbon atom of the CO_2 molecule, which exhibits Lewis acidity, with the transition metal [structure (IX)] is possible for metals in low oxidation states, which have an enhanced electron density. The adducts of transition metal complexes with Lewis acids containing the

"metal–Lewis acid" bond have a similar structure[20]. For example, the interaction of $(Ph_3P)_2Ir(CO)Cl$ with BF_3 leads to an adduct with a donor–acceptor Ir–BF_3 bond[87].

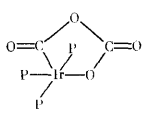
The complexes of transition metals in the lowest oxidation states, containing CO_2, can have the structure (X), which presupposes the interaction of the metal with the π-bond in CO_2. A third type of coordination is possible in the presence of a Lewis acidity centre in the coordination sphere or outside it [structure (XI)], where A is a Lewis acidity centre, which interacts with one of the oxygen atoms of the coordinated CO_2. Such interaction usually leads to the irreversible coordination of CO_2 in the form of carbonate, acetate, etc. Structure (XII) illustrates the interaction of the transition metal in the highest oxidation states, which is electron-deficient, with the weakly basic oxygen atom in CO_2. Such interaction between the transition metal and CO_2 is the least probable.

To date, X-ray diffraction studies have been carried out on only a few complexes containing CO_2 as the ligand. The structure of a complex containing CO_2 was first investigated by Aresta et al.[88] It was found that the P_2NiCO_2 fragment of the complex $[L_2Ni(CO_2)].0.75C_6H_5CH_3$, where $L = P(C_6H_{11})_3$, is located in a single plane:

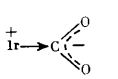


while CO_2 is linked to the nickel atom by a π-bond [see structure (X)]. The non-coordinated C–O bond has a length of 1.17 Å, which differs little from the length of the C–O bond in the free CO_2 molecule (1.16 Å), while the coordinated C–O bond has a length of 1.22 Å, which is much less than the length of a single C–O bond (1.45 Å); the OCO angle is 133°. Carbon dioxide is weakly bound in this complex and can be readily removed on passing argon through a solution of the complex in toluene at 25 °C; the initial complex is reformed on saturation of the solution with CO_2.

The structure of the complex $L_3Ir(CO_2)_2Cl$, where $L = P(CH_3)_3$, has also been established by X-ray diffraction[89]. Iridium has an octahedral coordination and the Ir–C and Ir–O bonds as well as a five-membered chelate ring formed by two CO_2 molecule were identified in the complex:



Thus CO_2 is coordinated in the given instance to the transition metal and the Lewis acid centre [see structure (XI)]. It has been suggested[89] that the complex is formed following the electrophilic attack by the carbon of the CO_2 group on the iridium atom with the subsequent analogous electrophilic attack by a second CO_2 molecule on the oxygen atom of the coordinated CO_2 and the closure of the organometallic ring. The replacement of the $P(CH_3)_3$ ligands by the chelating ligands $(CH_3)_2PCH_2CH_2P(CH_3)_2$(dmpe) in the above complex hinders the coordination of two CO_2 molecules. This results in the formation of the complex $(dmpe)_2Ir(CO_2)Cl$, for which the following mode of coordination of CO_2 has been proposed [see structure (IX)]:[90]



The structure of the complex $[Co(pr\text{-}Salen)K(CO_2)THF]_n$, where pr-Salen is *N,N'*-di(7-propylsalicylidene)ethylenediamine, has been studied recently[91]. In this polymeric complex CO_2 is coordinated to Co via the carbon atom, and one oxygen atom is linked to two potassium atoms, the other oxygen atom being linked to one potassium atom. Thus, in this instance CO_2 is bound to the transition metal via the carbon atom and there is additional coordination to the Lewis acidity centre (K^+) via the oxygen atoms. The lengths of the C–O bonds in the coordinated CO_2 molecule are 1.22 and 1.24 Å, while the OCO angle is 135 °C.

CO_2 is coordinated in an unusual manner in the $[HOs_3.(CO)_{10}(\mu\text{-}CO_2)Os_6(CO)_{17}]^-$ cluster[92]. The carbon atom of the CO_2 ligand is bound to the Os_6 cluster and the two oxygen atoms are found to the Os_3 cluster. The lengths of the C–O bonds in the CO_2 bridging ligand are 1.28 and 1.36 Å. It has been suggested[92] that the Os_6–C fragment can be regarded as a coordinated carbene and the coordination of the two oxygen atoms of the CO_2 ligand with the Os_3 cluster resembles that of a carboxylate ligand.

Thus the structures of only four complexes containing a coordinated CO_2 molecule have been reliably established by X-ray diffraction, CO_2 being coordinated in the complex in accordance with Schemes (IX)–(XI). The coordination of carbon dioxide to the transition metal alters its configuration. In all cases the OCO angle of the CO_2 ligand differs appreciably from 180° characteristic of the free CO_2 molecule. In certain cases the length of the C–O bond increases significantly. Evidently such marked changes in the structure of the CO_2 molecule as well as the redistribution of electron density induced by the interaction with the transition metal are associated with the activation of carbon dioxide. Since CO_2 is a fairly labile ligand, the preparation of the transition metal complexes of CO_2 must be based on initial coordination-unsaturated complexes.

2. The Reduction of Carbon Dioxide in the Presence of Transition Metal Complexes

The reactions involving the insertion of carbon dioxide in M–H or M–C bonds are apparently intermediate reactions in catalytic cycles leading to the reduction of CO_2. Unfortunately the mechanisms of these processes have not been investigated. The following schemes can therefore be proposed for the given reactions[8,9]:

$$LM{-}CO_2 \xrightarrow{X} LM{-}(CO_2){-}X\,, \qquad (1)$$

$$X{-}CO_2 \xrightarrow{LM} LM{-}(CO_2){-}X\,, \qquad (2)$$

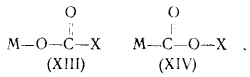
$$LM{-}X \xrightarrow{CO_2} LM\begin{matrix}X\\ \diagdown\\ \diagup\\ CO_2\end{matrix} \rightarrow LM{-}(CO_2){-}X\,, \qquad (3)$$

$$LM{-}X \xrightarrow{CO_2} LM{-}X{-}CO_2 \rightarrow LM\ CO_2X^{\ominus} \rightarrow LM{-}(CO_2){-}X\,, \qquad (4)$$

where LM is the transition metal complex and X = H or alkyl. The reaction involves three reactants: the transition metal complex, the ligand (H or R), and CO_2. Two of these can initially react with one another and then with a third reactant. Scheme (1) corresponds to attack by the free ligand on the coordinated carbon dioxide. Scheme (2) leads to an insertion product via the formation of an adduct of CO_2 with the ligand and its stabilisation on the transition metal. Both these schemes presuppose the presence of the free ligand in the reaction mixture. If the metal–ligand bond (M–H or M–R) is formed, the CO_2 molecule can be either coordinated to the coordination-unsaturated metal centre with subsequent migration of the ligand to the bound CO_2 [Scheme (3)] or can

attack directly the bound ligand with the intermediate formation of an ion pair [Scheme (4)].

There are two possible variants of the structure of the insertion product depending on the polarity of the M–X bond[8,9]:



(XIII) (XIV)

This entails the formation of a formate complex (XIII) or metal-carboxylic acids or their esters (XIV). The first of these reactions can serve as a basis for the catalytic reduction of CO_2 by hydrogen with formation of formic acid, methanol, and other products. In most of the known reactions involving the insertion of CO_2 in an M–H or M–C bond, formate complexes are formed. The insertion of CO_2 in a transition metal–hydrogen bond was observed for the first time in relation to the cobalt complex $(Ph_3P)_3Co(N_2)H$;[93] the cobalt formate complex $(Ph_3P)_nCoOOCH$ is formed in benzene at 25 °C and a CO_2 pressure of 1 atm. A similar formate complex has been obtained also from $(Ph_3P)_3CoH_3$.[94] The presence of the formate group in the complex has been confirmed by treatment with methyl iodide, which leads to the formation of methyl formate. In addition, treatment of the complexes with concentrated sulphuric acid leads to the evolution of CO; complexes of carbon dioxide evolve CO_2 under these conditions.

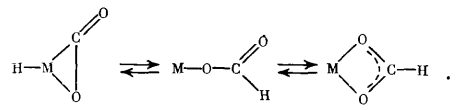
It is noteworthy that the reactions with sulphuric acid or methyl iodide constitute a kind of test and help to distinguish formate complexes from complexes with CO_2, which have very similar infrared spectra. As for the transition metal complexes with CO_2, the structure of the formate complexes has been established reliably by X-ray diffraction only in isolated cases. The structure of the ruthenium complex $(Ph_3P)_3$. .Ru(H)OOCH has been described[95]. In the crystalline form, the compound contains a formate group in which hydrogen is located in the *trans*-position relative to this group. This complex was obtained by the reaction of CO_2 with a solution of $(Ph_3P)_4RuH_2$ in toluene at 25 °C at 1 atm [96] or with solutions of $(Ph_3P)_3RuH_4$ and $(Ph_3P)_3Ru(N_2)H_2$.[97] The reactions of the above complex in solution are extremely unusual for formate complexes and are more consistent with the complex of ruthenium hydride and CO_2 of the type $(Ph_3P)_3Ru(CO_2)H_2$. For example, the reactions with Ph_3P, N_2, H_2, or CO are accompanied by the elimination of CO_2 under mild conditions[97]:

$$(Ph_3P)_3\,Ru\,(H)\,OOCH \xrightarrow{L} (Ph_3P)_3\,Ru\,(L)\,H_2 + CO_2\ ;$$
$$L = Ph_3P,\ N_2,\ H_2,\ CO\ .$$

The hypothesis of the formation of the ruthenium hydride complex with CO_2 has been confirmed by ^1H NMR study of a solution in the ruthenium formate complex $[Ph(CH_3)_2P]_4$. .Ru(OOCH)$^+$.[98]

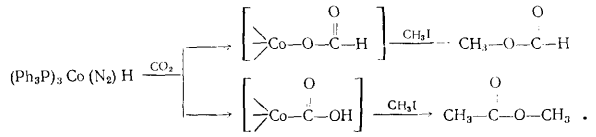
The iron formate complex $L_2Fe(OOCH)_2$, where $L = Ph(C_2H_5)_2P$ or $Ph_2(C_2H_5)P$, is formed when the solid complexes L_3FeH_4 or $L_3Fe(N_2)H_2$ are irradiated with visible light in an atmosphere of CO_2;[99] the formation of the formate complex is not observed in the absence of irradiation. The authors[99] suggest that the reaction is induced by the photochemical dissociation of the H_2 or N_2 ligand.

In all cases of the formation of formate complexes, it has been suggested that the first stage of the reaction is coordination of CO_2 to the transition metal atom, which requires the presence of a coordination-unsaturated complex with an enhanced electron density at the transition metal atom. Like the complexes containing CO_2, formate complexes can therefore be obtained only when the molecule of the initial complex containing labile ligands (N_2, H_2, Ph_3P), whose dissociation leads to coordination-unsaturated complexes. The formate complexes are apparently formed from the hydride complex with CO_2 as a result of the migration of the hydride to the carbon atom of the CO_2 molecule:



This reaction is in most cases reversible. For example, the ruthenium complex $(Ph_3P)_3Ru(H)OOCH$ contains the formate ligand in the solid state[95], while on its dissolution in CH_2Cl_2 a complex containing carbon dioxide is formed: $(Ph_3P)_3Ru$. .$(H_2)CO_2$.[97,98]

Together with the formation of formate complexes following the insertion of CO_2 in an M–H bond, a metal-carboxylic acid can also be produced. The interaction of CO_2 with $(Ph_3P)_3Co(N_2)H$ and subsequent methylation of the reaction products with CH_3I entail the formation of both methyl formate and methyl acetate (approximately 17%):[100]



Thus the interaction of carbon dioxide with transition metal hydride complexes leads to its reduction. This reaction is apparently the key stage in the reduction of CO_2 by hydrogen to give organic compounds.

Instances of the conversion of the formate complexes into carbonyl hydride complexes are known. For example, $(Ph_3P)_3Rh(OOCH)H$ is converted into $(Ph_3P)_3Ru(CO)H_2$ on heating[95]. In the presence of silicon or aluminium hydrides and ruthenium and rhodium complexes, CO_2 is reduced in benzene to CO:[101]

$$(Ph_3P)_3\,MCl + HSi\,(OC_2H_5)_3 \xrightarrow{CO_2\,(1\,atm)} (Ph_3P)_2\,M\,(CO)\,Cl\ ;$$
$$M = Rh,\ Ru\ .$$

The yield of CO is one mole per mole of the complex. HSi. .$(C_2H_5)_3$, $H_2Si(C_3H_7)_2$, and $LiAlH_4$ can be used as the reductants. It has been suggested[8,101] that in the first stage the silane adds to the complex via the oxidative addition mechanism with formation of a metal–hydrogen bond, after which CO_2 is inserted in this bond with formation of a formate ligand, whose decomposition leads to the formation of carbonyl complexes. The interaction of CO_2 with transition metal hydrides complexes also leads to carbonyl complexes[97,102]. The ruthenium complex $(Ph_3P)_4RuH_2$ reacts with CO_2 at 130 °C and a pressure of 20 atm to form $(Ph_3P)_3Ru(CO)H_2$.[97] The reaction with $[Ph_2(CH_3)P]_4WH_4$ takes place under milder conditions. The refluxing of a solution of this complex in toluene in a CO_2 atmosphere results in the formation of $[Ph_2(CH_3)P]_3W(CO)_3$ (yield 60%).[102] The reduction of CO_2 to CO can be achieved using H_2 as the reductant,[103] i.e.

$$(Ph_3P)_3\,RhCl + CO_2 + H_2 \xrightarrow[100^\circ C]{(40\ atm)} (Ph_3P)_2\,Rh\,(CO)\,Cl + H_2O + Ph_3P\ ,$$

and hexamethylphosphoramide as the solvent. The reaction is appreciably accelerated by the addition of water. It has been suggested[103] that formic acid is formed initially and then decomposes to CO and H_2O.

The disproportionation and deoxygenation of CO_2 in the presence of titanium and zirconium complexes have been described[104]:

$$[(C_5H_5)_2\,TiCl]_2 + CO_2 \xrightarrow[90^\circ C]{10\ atm} [(C_5H_5)_2\,TiCl]_2O + CO\ ,$$

$$4\,(C_5H_5)_2\,Ti\,(CO)_2 + 4{}^{13}CO_2 \xrightarrow[50^\circ C]{1\ atm} [[(C_5H_5)_2\,Ti]_2\,(^{13}CO_3)]_2 + 2{}^{13}CO + 8CO\ ,$$

$$3\,(C_5H_5)_2\,Zr\,(CO)_2 + 3CO_2 \xrightarrow[70^\circ C]{1\ atm} [(C_5H_5)_2\,ZrO]_3 + 9CO\ .$$

The disproportionation of CO_2 in the presence of carbonylmetallate anions has been investigated[105]:

$$2Na[(C_5H_5)Fe(CO)_2] + CO_2 \rightarrow [(C_5H_5)Fe(CO)_2]_2 + Na_2CO_3 + CO .$$

The use of $^{13}CO_2$ made it possible to demonstrate that the disproportionation of CO_2 proceeds in accordance with the mechanism

$$2CO_2 + 2e \rightarrow CO_3^{2-} + CO .$$

The authors[105] suggest that two CO_2 molecules are coordinated to the initial complex $Na[(C_5H_5)Fe(CO)_2]$ in the first stage of the reaction with the subsequent formation of Na_2CO_3 and $[(C_5H_5)Fe(CO)_3]^+$; the latter reacts rapidly with the excess of $[(C_5H_5)Fe(CO)_2]^-$ anions to form a dimer.

The example of the non-catalytic reduction of CO_2 to a formate ligand or to CO presented above can be regarded as models of the individual stages of catalytic processes involving CO_2. It is noteworthy that the reduction of carbon dioxide to CO or HCOOH is thermodynamically unfavourable at low temperatures and pressures. It therefore occurs only when the product can bind strongly to the transition metal.

3. Catalytic Reduction of Carbon Dioxide

Catalytic reactions based on CO_2 constitute a field of organic chemistry which has been little studied. Several investigations have been devoted to the synthesis of alkyl formates or formamides from CO_2, H_2, an alcohol, or an amine[106,107]. It has been shown[100] that methyl formate is formed from CO_2, H_2, and CH_3OH at 60 atm and 100 °C:

$$CO_2 + H_2 + CH_3OH \rightarrow HCOOCH_3 + H_2O .$$

Since the reaction involving the formation of HCOOH from CO_2 and H_2 is thermodynamically unfavourable under mild conditions, the authors added alkylating agents (CH_3I and a solution of BF_3 in CH_3OH) to the reaction mixture in order to shift the equilibrium. $(Ph_3P)_3IrH_3$ and $(Ph_3P)_3Ru(H)Cl$ showed the highest catalytic activity. Subsequently Japanese investigators obtained alkyl formates from CO_2, H_2 and alcohols (CH_3OH, C_2H_5OH, and C_3H_7OH) at 50 atm and 140 °C in the presence of $(Ph_2PCH_2CH_2PPh_2)_2Pd$ and $(Ph_3P)_4RuH_2$ and added amines [$(C_2H_5)_3N$, etc.].[107] The yield of alkyl formate reached 50 moles per mole of the catalyst. At a pressure of the CO_2–H_2 mixture of 50 atm and at room temperature, the formation of HCOOH in an amount up to 40 moles per mole of the catalyst was observed in the presence of $(Ph_2PCH_2CH_2.PPh_2)_2Pd$ and $(C_2H_5)_3N$. The addition of water to the reaction mixture increases significantly the yield of formic acid[108]. It has been shown[109] that the carbonylmetallate anions $[HFe(CO)_4]^-$ and $[HFe_3(CO)_{11}]^-$ also catalyse the synthesis of alkyl formates from CO_2, H_2, and an alcohol.

Secondary amines interact with CO_2 and H_2 at 50–60 atm and 100–125 °C to form dialkylformamides[9]:

$$CO_2 + H_2 + R_2NH \rightarrow HCONR_2 + H_2O .$$

The most active catalysts are $(Ph_2PCH_2CH_2PPh_2)_2Pd$, $(Ph_3P)_2Ir(CO)Cl$, and $(Ph_3P)_3CuCl$, in the presence of which the yield reaches 800–1200 moles of dimethylformamide per mole of the catalyst.

In protic media, vanadium, titanium, molybdenum, and tungsten complexes catalyse the reduction of CO_2 by zinc and aluminium amalgams to HCOOH, HCOH, CH_3OH and in certain cases also to CH_4 at a CO_2 pressure of 1–5 atm and 20 °C;[110,111] the yields amount to several moles per mole of the catalyst.

At 150 °C and 1 atm the L_nRh_m–$AlBr_3$ system, where $L_nRh_m = Rh_4(CO)_{12}$, $[Rh(CO)_2Cl]_2$, or $(Ph_3P)_3RhCl$, catalyses the reduction of CO_2 by hydrogen to carbon monoxide[112]. The yield of CO ranged from 9 to 11 moles of CO per gramme-atom of rhodium. In addition, traces of C_1–C_3 alkanes were detected in the gas phase and the dissolution of the solid phase in THF led to solutions whose infrared spectra (absorption bands at 1981 and 2059 cm^{-1}) corresponded to the anions $[Rh(CO)_2X_2]^-$, where X = Cl or Br. In the absence of the rhodium complex or H_2, there was no reduction of CO_2. It has been suggested[112] that a hydride-containing rhodium complex with CO_2 is formed in the given instance and that $AlBr_3$ apparently activates the coordinated CO_2 molecule. The introduction of metallic aluminium into the given system has resulted in a sharp increase in the yields of hydrocarbons under the same conditions (see Table 2).[73]

An increased content of aluminium in the $Rh_4(CO)_{12}$–$AlBr_3$–Al system gives results analogous to those in the synthesis of alkanes from CO and H_2 in the presence of the same system[73]. In the range of Al : $AlBr_3$ ratios from 0 to 0.1, the content of C_1–C_4 alkanes increases and there is a sharp decrease of the CO concentrations in the products of the synthesis. In the absence of metallic aluminium, CO_2 is reduced only to CO and the yields of alkanes are low (Table 2). The introduction of aluminium accelerates the reduction of CO to alkanes[72], which leads in its turn to a decrease of the CO concentration in the products of the synthesis.

Table 2. The degrees of conversion of carbon dioxide (K_{CO_2}, mol CO_2/g-atom Rh) and the compositions of the reaction products (vol.%) in the synthesis of alkanes from CO_2 and H_2 in the presence of rhodium complexes.

L_nRh_m	K_{CO_2}	Reaction products, vol.%					
		CO	CH_4	C_2H_6	C_3H_8	iso-C_4H_{10}	n-C_4H_{10}
$Rh_4(CO)_{12}$	9	0	64	9	5	21	1
$[Rh(CO)_2Cl]_2$	8	0	68	7	4	20	1
$(Ph_3P)_2Rh(CO)Cl$	6	0	73	8	4	15	0
$(Ph_3P)_3RhCl$	6	0	73	11	4	12	0
$RhCl_3 \cdot 3H_2O$	2	14	60	9	5	12	0
$Rh_4(CO)_{12}$	8	98	1	0.5	0.5	0	0

Note: Reaction time 20 h; the remaining conditions were the same as in Table 1. The last row presents data obtained in the absence of metallic aluminium.

The catalytic properties of the L_nRh_m–$AlBr_3$–Al system are significantly influenced by the structure of the rhodium compound (Table 2).[73] The compositions of the reaction products are extremely similar for all the rhodium complexes investigated but they are different from those obtained in the presence of $RhCl_3$. Thus the presence of ligands (CO and Ph_3P) in the molecule of the initial complex results, as in the reduction of CO (Table 1), in the formation of systems exhibiting a higher catalytic activity in the reduction of CO_2 than that of the $RhCl_3$–$AlBr_3$–Al system.

The synthesis of C_1–C_2 hydrocarbons and dimethyl ether from CO_2 and H_2 at 1 atm and 300–400 °C in the presence of graphite layer compounds with a transition metal (Mo, W, Co, Ni, Pd, Pt, Fe) and an alkali metal (K, Na), has been described[113].

Methanol has been obtained from CO_2 and H_2 in the presence of $SnCl_4$ at 200 °C and a pressure of 100 atm (1 : 3 CO_2–H_2 mixture).[114] The yield of methanol was 8.2% for a degree of conversion of CO_2 of 8.8%. Together with the synthesis of methanol, the authors[114] observed the formation of small amounts of CO at 200–300 °C.

These few examples exhaust the number of catalytic reactions involving the reduction of CO_2 in the presence of transition metal complexes. In most cases the mechanisms of the reactions of CO_2 with a transition metal and of the activation of the coordinated carbon dioxide molecule have not so far been established.

The data examined permit the conclusion that the development of metal complex catalysts for the synthesis of hydrocarbons from carbon oxides and hydrogen is so far feasible on a purely laboratory scale. The systems obtained cannot serve as a basis for the creation of catalysts of practical importance. On the other hand, the mechanisms of processes involving transition metal complexes and those in the presence of heterogeneous catalysts have much in common in many instances. The study of metal complex catalysts for the reduction of carbon oxides can therefore prove useful both for the development of new industrial catalysts for the synthesis of hydrocarbons from mixtures of carbon oxides and hydrogen and for the improvement of the existing ones.

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Zelinskii Institute of
Organic Chemistry,
USSR Academy of
Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 948-970 (1984) U.D.C. 541.127:833.220

Solvation Effects and the Mechanism of the Heterolysis of t-Butyl Halides

G.F.Dvorko, E.A.Ponomareva, and N.I.Kulik

Data on the kinetics and mechanism of the heterolysis of t-BuX (X = Cl, Br, I) in the gas phase and in individual solvents are surveyed. The mechanism of the unimolecular heterolysis of t-BuX and the role of the solvent in this process are discussed. The bibliography includes 192 references.

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I. INTRODUCTION

The reactions involving the unimolecular heterolysis of t-BuX (unimolecular solvolysis, S_N1, $E1$) have attracted the attention of chemists for more than 40 years[1-6]:

$$\text{t-BuX} \xrightarrow{\text{ROH}} \begin{cases} \text{t-BuOR} + \text{HX} \\ \text{Me}_2\text{C}{=}\text{CH}_2 + \text{HX} \end{cases}.$$

Both substitution and elimination products are formed in proton-donating solvents, while in the gas phase and in aprotic solvents only elimination products are obtained. These reactions have been widely used in the study of the mechanism of the heterolytic cleavage of a covalent bond and of the influence of the solvent on the process. The principal data on the mechanisms of these reactions can be found in any modern text-book or monograph on organic or physical organic chemistry (see, for example, Refs.7-13). More detailed data are available in reviews of the solvolysis of organic substrates[1,5,14-17] and of the influence of the solvent on heterolytic reactions[4,6,18-24]. The number of publications on this problem has rapidly increased recently, novel research techniques have appeared, and new approaches to the interpretation of the results have been devised; at the same time contradictions have also accumulated.

The aim of the present review is a critical survey of modern ideas concerning the mechanism of the heterolysis of t-BuX. Attention has been concentrated on the effect of the solvent. Virtually all the available experimental kinetic parameters for the heterolysis of t-BuX (X = Cl, Br, I, or F) and certain other t-butyl derivatives in the gas phase and in individual solvents have been compiled and tabulated in the present review. A correlation analysis of the influence of various solvent parameters (nucleophilicity, electrophilicity, polarity, polarisability, and the energy of the self-association of the solvent) on the rate of heterolysis of t-BuX (X = Cl, Br, or I) has been carried out. This permits a critical approach to the interpretation of the solvent effect and certain new conclusions about the reaction mechanism.

II. THE NATURE OF THE TRANSITION STATE

The very extensive data on the heterolytic reactions of t-BuX are usually surveyed on the basis of the same, at first sight simple, mechanism, according to which a cationoid intermediate (an ion pair or a carbonium ion) is formed in the rate-limiting stage from t-BuX and is then rapidly converted into the reaction products.

The rates of these reactions increase rapidly with increase of solvent polarity; in the case of t-BuCl, the increase is by ~15 orders of magnitude on passing from n-heptane to water (Table 1) (t-BuCl is used as a standard in the correlation of the rates of solvolysis of other substrates—see the Grunwald–Winstein equation[1-3,14,15,18,21,23,25]).

Marked charge separation takes place in the transition state of the heterolysis of t-BuX:[1-6,10,23,26,27] 0.8 of an electron[4,26,28], $\mu^{\neq} = 8.8$ D, $d^{\neq} = 2.3$ Å.[26] In hydroxyl-containing solvents $\mu^{\neq}$ increases markedly[4,23]. On passing from the initial to the transition state, the volume of t-BuCl increases from 111 to 116 $cm^3\ mol^{-1}$;[6] however, the volume of activation diminishes as a result of electrostriction: $\Delta V^{\neq} \cong -20$ $cm^3\ mol^{-1}$.[29] $Me_4N^+Cl^-$ is used as a model of the transition state[18]. The appreciable charge separation in the transition state is indicated by the reaction constant[30] for the heterolysis of $RCMe_2Cl$ in the Taft equation [$\rho = -3.3$ in 80% ethanol (EtOH) [31] and $\rho = -3.6$ in dimethylformamide (DMF) [32]]. The agreement between the experimental β-deuterium kinetic isotope effect in the solvolysis of t-BuCl [33] and the calculated H–D effect for the formation of t-Bu^+ ($k_{C_4H_9Cl}/k_{C_4D_9Cl} \cong 2.4$) [34] as well as the slope (~0.9) of the relation between the free energies of activation for the solvolytic reactions of alkyl chlorides and their heats of ionisation[35] are consistent with this finding.

The rate of solvolysis of t-BuCl depends on the nature of the solvent approximately in the same way as the rate of addition of Br_2 to styrene and phenylacetylene[36], which indicates a high polarity of the transition state in all cases. We may note that the calculations based on the ^{14}C and ^{37}Cl kinetic isotope effects lead to a less polar transition state[37-39], although it is believed[40] that the small isotope effect of chlorine (~1.01) in the solvolysis of t-BuCl is associated with the intense solvation of the anion formed and not with the low polarity of the transition state.

The effects of the solvent and salts[41,42] indicate the formation of a highly polar transition state[4,6,43], although in the case of Ph_2CHX these effects are more marked than for t-BuX.[16,44-46] The heterolysis of diphenylmethyl derivatives usually results in the formation of intermediate carbonium ions and solvent-separated ion pairs[16,45,47]. In the reaction involving t-BuX, less polar intermediates are apparently produced. Evidence has been adduced[6,18,19] in support of the view that the polarity of the transition state in the heterolysis of t-BuCl decreases with decrease of the polarity of the medium; however, other investigators believe[46,48] that the polarity of the transition state is independent of the nature of the medium. The possibility of the formation of a four-membered transition state in the heterolysis of t-BuCl in solvents of low polarity has been discussed[4,26,48,49].

Table 1. The logarithms of the rate constants for the heterolysis of t-BuX and solvent parameters.

No.	Solvent	$-\lg k^{25}$ (s^{-1})			ε^{20}	n_D^{20}	B	E	E_T	DN	AN	δ^2	Refs.
		X = Cl	X = Br	X = I									
1	Gas phase	19.3[a]	16.8[a]	14.3[a]	1.00	1.0000	0.00	0.00	0.00	—	—	0.00	[123]
2	H_2O	1.54	0.119	−0.188	80.1	1.3330	156	21.8	63.1	18.0	54.8	0.592	[124]
3	MeOH	6.06	4.46	3.90	32.7	1.3286	218	14.9	55.5	18.9[b]	41.3	0.196	[125]
4	EtOH	7.07	5.36	—	24.3	1.3614	235	11.6	51.9	19.2[b]	37.1	0.158	[126, 18]
5	n-BuOH	7.52[c]	—	—	17.3	1.3992	231	10.3	50.2	19.5[b]	—	0.112	[127]
6	iso-PrOH	7.80	6.07	—	18.3	1.3773	236	8.7	48.6	19.8[b]	33.5	0.130	[128, 71]
7	t-BuOH	8.30[t]	4.97	—	10.9	1.3848	247	5.2	43.9	21.5[d]	—	0.113	[128, 129]
8	n-HexOH	7.91[f]	—	—	12.5	1.4182	230	10.5	51.5	—	—	0.112	[127]
9	n-OctOH	8.18[g]	—	—	10.3	1.4291	230	10.8	51.8	—	—	0.111	[127]
10	CF_3CH_2OH	3.98	2.62	—	26.5	1.2907	—	—	59.5	—	23.3	—	[84, 130]
11	CH_2OHCH_2OH	4.60	—	—	38.7	1.4318	224	15.0	56.3	—	—	0.318	[128]
12	Glycerol	4.10	—	—	42.5[e]	1.4735[e]	—	—	57.0	—	—	—	[131]
13	PhOH	4.65[h]	—	—	10.3	1.5418	130	13.7	54.8	—	—	0.107	[62, 132]
14	HCO_2H	2.96	2.02	—	57.9	1.3714	131	16.7	57.9	11.4[d]	83.6	0.138	[25, 126]
15	CF_3CO_2H	3.19	—	—	39.0	1.2850	—	—	—	—	105.3	—	[133]
16	CH_3CO_2H	6.70	5.52	—	6.15	1.3716	139	14.6	51.2	12.1[d]	52.9	0.154	[128, 127, 134]
17	NH_3	7.26	—	—	16.9	1.3250	443	10.6	51.7	59	—	0.212	[135]
18	$PhNH_2$	6.13	—	—	6.89	1.5855	346	6.2	44.3	26.3[d]	—	0.107	[136]
19	$HCONH_2$	4.33	—	—	112	1.4475	270	14.5	56.6	22.2[d]	39.8	0.400	[137]
20	HCONHMe	6.54	—	—	190	1.4310	287	11.9	54.1	—	—	0.255	[106]
21	MeCONHMe	7.33	—	—	179[i]	1.4301	338	9.9	52.0	—	—	0.250	[106]
22	EtCONHMe	8.00	5.65[j]	—	166	1.4350	—	—	—	—	—	—	[41, 128]
23	DMF	8.62	5.62[k]	—	36.7	1.4272	291	2.6	43.8	26.6	16.0	0.198	[106, 113]
24	Dimethylacetamide	9.31	—	—	37.8	1.4356	343	2.4	43.7	27.8	13.6	0.199	[106]
25	*N*-Methylpyrrolidinone	8.97[l]	6.00[m]	—	32.2[e]	1.4680	319	1.3	42.2	27.3	—	0.121	[65]
26	Propylene carbonate	8.29	5.50	4.02	70.0	1.4189	180	6.1	46.6	15.1	18.3	0.138	[102]
27	$MeNO_2$	8.12	5.44[n]	—	38.6	1.3819	65	5.1	46.3	2.7	20.5	0.170	[62, 138]
28	MeCN	8.64	5.90[o]	4.28	37.5	1.3416	160	5.2	46.0	14.1	19.3	0.150	[119]
29	Me_2CO	9.61[p]	7.13[r]	5.21	20.7	1.3588	224	2.1	42.2	17.0	12.5	0.095	[139]
30	Ac_2O	8.32	—	—	20.5	1.3904	100	3.7	43.9	10.5	—	0.141	[128]
31	$PhNO_2$	9.72[s]	6.95	5.52	34.8	1.5546	67	0.0	42.0	4.4	14.8	0.113	[140, 141]
32	PhCN	—	7.11	5.43	25.2	1.5282	155	0.0	42.0	11.9	15.5	0.123	[141]
33	$PhCF_3$	—	—	6.10	9.18[i]	1.4146	—	0.0	—	—	—	—	[141]
34	C_6H_6	—	—	6.56	2.28	1.5011	48	2.1	34.5	0.1	8.2	0.085	[141]
35	PhF	—	—	6.58	5.42	1.4657	38	0.0	38.1	—	—	0.076	[141]
36	PhCl	—	—	6.58	5.62	1.5218	38	0.0	37.5	0.6	—	0.087	[141]
37	PhBr	—	—	6.59	5.40	1.5560	40	0.0	37.5	0.2	—	0.096	[141]
38	PhI	—	—	6.51	4.62	1.6212	38	0.0	37.9	0.0	—	0.084	[141]
39	PhOMe	—	—	6.37	4.33	1.5170	255	1.4	37.2	19.8	—	0.097	[141]
40	$PhCH_3$	—	—	7.04	2.38	1.4969	58	1.3	33.9	2.9	—	0.080	[141]
41	CH_2Cl_2	9.54	7.21	6.12	9.08	1.4246	23	2.7	41.1	1.1[d]	20.4	0.095	[142]
42	CH_2ClCH_2Cl	—	7.75	6.15	10.4	1.4451	40	3.0	41.9	0.1	—	0.108	[142]
43	CH_2BrCH_2Br	—	—	7.09	4.78[e]	1.5387	—	—	—	—	—	—	[142]
44	t-BuCl	13.6[u]	—	—	9.96	1.3856	64	—	—	—	—	—	[143]
45	Dioxan	10.8	8.52	6.78	2.21	1.4424	237	4.2	36.0	14.8[v]	10.8	0.110	[71, 128, 144]
46	THF	—	—	6.57	7.39	1.4076	287	0.0	37.4	20.0	8.0	0.076	[144]
47	Et_2O	12.7[w]	—	—	4.35	1.3527	280	0.0	34.6	19.2	3.9	0.057	[18]
48	$(CO_2Et)_2$	—	7.54	6.18	8.08	1.4112	—	—	—	—	—	—	[144]
49	$PhCO_2Et$	—	—	6.83	6.02	1.5052	142	—	—	—	—	—	[144]
50	$MeCO_2Et$	—	—	7.02	6.02	1.3724	181	1.6	38.1	17.1	—	0.082	[144]
51	n-Heptane	16.0[x]	—	—	1.92	1.3877	0.0	0.0	30.9	0.0	0.0	0.060	[145]

Remarks. The main bulk of the values of ε, n, B, E, E_T, DN, AN, and δ^2 were taken from Refs. 6, 11, 21, 22, 90, and 91 (see Section IV).

[a] Calculated from the values of k at 230–680 °C. [b] Taken from Kanevskii and Zarubina[146]. [c] $\lg k^{25} = -7.26$ in the paper of Rudakov and Kozhevnikov[48]. [d] Taken from Makitra and Pirig[147]. [e] At 25 °C. [f] $\lg k^{25} = -7.43$ in the paper of Rudakov and Kozhevnikov[48]. [g] $\lg k^{25} = -7.52$ in the paper of Rudakov and Kozhevnikov[48]. [h] Calculation from the values of k at 40°, 50°, and 55 °C. [i] At 30 °C. [j] Calculation from the values at 24.8°, 39.2°, and 50.7 °C. [k] $\lg k^{25} = -5.66$ in the paper of Peters and Anteunis[32]. [l] Estimate from $k^{60} = 9.1 \times 10^{-8}$ s^{-1}, $\Delta H^{\neq} = 102.1$ kJ mol^{-1}.[16] [m] Calculation from the values of k at 20°, 40°, and 60 °C for [HBr] ≅ 0.0275 M. [n] $\lg k^{25} = -5.36$ in the paper of de la Mare et al.[118] [o] $\lg k^{24.5} = -5.92$ in Hoffman's paper[117]. [p] $\lg k^{25} = -9.9$ in Rudakov's paper[128]. [r] Calculation from the values of k at 20°. 40°, 44.4°, 50°, and 60 °C, taken from Winstein et al.[68], yields $\lg k^{25} = -7.16$. [s] Calculation from the values of k at 39°, 53°, and 70 °C.[140] [t] Calculation from the values of k at 27–60 °C, taken from Viana and Concalves[129], yields $\lg k^{25} = -5.3$. [u] Calculation from the values of k at 100° and 120 °C, taken from Koppel[145], yields $\lg k^{25} = -10.0$. [v] Taken from Gutman[90]. [w] Estimate in Abraham's paper[18] from data for 120 °C.[4] $\lg k^{25} = -10.4$ in the paper of Pocker and Buchholz[148] and $\lg k^{120} = -7.0$ in the paper of Koppel and Palm[4]. If $\lg k^{25} = -12.7$ is used, then $\Delta H^{\neq} = 132.3$ kJ mol^{-1} and $\Delta S^{\neq} = -52.8$ J mol^{-1} K^{-1} (realistic values). If one uses $\lg k^{25} = -10.4$, then $\Delta H^{\neq} = 77.9$ kJ mol^{-1} and $\Delta S^{\neq} = -191.3$ J mol^{-1} K^{-1} (improbable values). [x] Estimate in Abraham's paper[6]: $\lg k^{25} = -13.5$.

The interpretation of the solvent effect is complicated by the fact that the solvent influences both the initial state of the substrate and the transition state and a difference between these effects has been observed[6,10,15,48]. The separate effects of the medium on the solvation of the initial and transition states are taken into account using a thermodynamic approach to the analysis of kinetic data[6,48,50]. Unfortunately this method does not differentiate the ionic intermediates formed in the heterolysis of a covalent bond; the polarity of the transition state is usually assumed to be constant for all media.

Comparative analysis of the Henry coefficients for the ground state and the rate constants for the solvolysis of t-BuCl showed[48] that the change in the rate of reaction in a medium of low polarity depends greatly on the degree of solvation of the transition state, while in a polar medium it depends on the degree of solvation of the substrate in the initial state. The use of the solubility parameter δ in combination with the free energies of activation enabled Abraham[6] to determine the free energies of the transition state in the heterolysis of t-BuCl(Br) in various solvents. It was shown that the decrease of the free energies of activation with increase of the polarity of the medium is due both to the increase of the energy of the initial state and the decrease of the energy of the transition state, the latter making the main contribution.

The correlation between the relative free energies of the transition state and the free energies of the model compound $Me_4N^+Cl^-$ showed that the polarity of the transition state is much higher in polar solvents than in solvents of low polarity. However, after the determination of the contribution of the energy of formation of a cavity (cage) in the solvent, Abraham recently abandoned this conclusion; he now believes that the polarity of the transition state is independent of the nature of the medium. On the basis of the concept of S_N1 transition states as ternary species formed from $t\text{-}Bu^+X^-$ and solvent molecules ($R^+...X^-...Solv$) or metal ions ($R^+...X^-...M^+$), Rudakov[50,51] analysed the influence of the medium on the rate of heterolysis of t-BuX and, having separated the effects of the solvation proper and the Coulombic interaction in the transition state, showed that the solvent effect is due mainly to the solvation of the transition state.

It is noteworthy that the solvation of the substrate in the initial state can greatly influence $\Delta H^{\neq}$ and $\Delta S^{\neq}$.[15] The initial state is less polar than the transition state and its solvation therefore depends greatly on the solvent structure[52,53].

It is usually believed that the heterolysis of t-BuX, interpreted within the framework of Winstein's scheme, stops at the stage involving the formation of a contact ion pair[54–57]:

$$t\text{-}BuX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} t\text{-}Bu^+X^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} t\text{-}Bu^+ \mid Solv \mid X^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} t\text{-}Bu^+ + X^-.$$

However, this is not always so. Since the solvolysis of t-BuX in proton-donating solvents proceeds via the S_N1 mechanism, t-BuOR should be formed from an intermediate carbonium ion or a solvent-separated ion pair (attack by the nucleophile on the contact ion pair would lead to S_N2 substitution)[14,16]. In water the yield of the olefin (~5%) is independent[58] of the nature of the departing group in t-BuX (X = Cl, Br, I, or SMe_2I), which indicates the formation of an intermediate carbonium ion; in acetic acid, ethanol[58], and methanol[59], the yield of the olefin increases with the basisity of the departing group, which indicates the formation of the olefin from intermediate ion pairs.

It is believed[60] that in solution in CF_3CH_2OH the contact ion pair is converted into a solvent-separated ion pair in the rate-limiting stage of the ionisation of t-butyl halide. The contact ion pairs were generated in solution in CF_3CH_2OH by the addition of HCl to isobutene[14,61]:

$$t\text{-}BuCl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} t\text{-}Bu^+Cl^- \overset{k_2}{\rightsquigarrow} t\text{-}Bu^+ \mid Solv \mid Cl^- \quad (\downarrow)$$
$$Me_2C{=}CH_2 + HCl \qquad t\text{-}BuOCH_2CF_3 .$$

The yield of the product of the reaction involving the reconversion of the ion pair (t-BuCl) was higher by a factor of two than the yield of the substitution product ($t\text{-}BuOCH_2CF_3$). Consequently $k_{-1} > k_2$ and the rate-limiting stage in the heterolysis of t-BuCl in CF_3CH_2OH should be the formation of a solvent-separated ion pair. The phenolysis of t-BuCl apparently proceeds partly via a carbonium ion—the rate of reaction diminishes in the presence of a salt with a common ion[62]. This is apparently a unique case, since the salt effect, associated with the operation of the Law of Mass Action, is not as a rule manifested in the solvolysis of t-BuX.[14,16] Possibly this effect may be important in methanol and dioxan[63].

The solvolysis of t-BuCl in formic acid proceeds at the same rate as the unimolecular exchange of the anion[64], which indicates the formation of an intermediate carbonium ion or a solvent-separated ion pair. The solvolysis of t-BuCl in *N*-methylpyrrolidinone in the presence of radioactive LiCl* is accompanied by the unimolecular exchange of the anion (~3%); the usual salt effect of the chloride observed under these conditions indicates the formation of an intermediate solvent-separated ion pair. The same intermediate is apparently formed in the solvolysis of 2-bromo-2-methylpentane in DMF.[32] The intermediate solvent-separated ion pair is apparently also formed in the methanolysis of 2,4-dimethylhex-4-yl phthalate, which proceeds with 54% retention of the configuration[66]. The exchange of the anion in t-BuCl, catlaysed by $FeCl_3$, apparently proceeds in benzene solution via a solvent-separated ion pair[67]. In acetone[68], $MeNO_2$,[69] and acetic acid[14], the anion derived from t-BuCl(Br) does not exchange; the specific salt effect of perchlorate is not manifested in acetic acid. Consequently in these and less polar solvents the main intermediates are contact ion pairs†.

Evidence showing that the reaction proceeds via a rate-limiting stage involving the formation of a contact ion pair in the heterolysis of t-BuBr in acetonitrile was obtained by a comparative study of the influence of added water and salts on the rates of the reactions of t-BuBr and Ph_2CHBr.[45] It is evident from the foregoing that in aprotic solvents the rate of reaction is as a rule limited by the stage involving the formation of a contact ion pair, while in proton-donating solvents the rate-limiting stage involves the conversion of the contact ion pair into a solvent-separated ion pair. The increase of the dipole moment of $[t\text{-}BuCl]^{\neq}$ on passing from aprotic to proton-donating solvents[4,23,26] and also Abraham's conclusion that the polarity of the transition state increases with increase of the polarity of the medium[6,18] are satisfactorily consistent with this finding.

The above view has been confirmed in a study[70] where the logarithms of the rate constants for the heterolysis of t-BuBr and Ph_2CHBr in various solvents were compared with the Kosower solvent polarities, Z. It was shown that in aprotic solvents the rates of heterolysis of both substrates are similar, while in proton-donating solvents t-BuBr reacts at a rate lower by 2.5 orders of magnitude (see Figure).

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†The heterolysis of t-BuCl(Br) in acetic acid apparently proceeds partly also via a solvent-separated ion pair, which is indicated by the formation of t-BuOAc in ~30% yield[58].

The Figure also shows that there is a linear relation between $\lg k_{Ph_2CHBr}$ and Z for the entire set of solvents, while the rate of heterolysis of t-BuBr deviates sharply from this relation in the region of the transition from aprotic to proton-donating solvents as a result of the decrease of the rate of reaction in isopropyl alcohol. The $\lg k_{Ph_2CHBr}$ are satisfactorily correlated with the values of Z (correlation coefficient 0.978), while in the case of t-BuBr the correlation is unsatisfactory[71]. This can be explained by a change of mechanism of the heterolysis of t-BuBr: in aprotic solvents the rate of the process is limited by the formation of a contact ion pair, while in proton-donating solvents it is limited by the formation of a solvent-separated pair. In the heterolysis of Ph_2CHBr the rate-limiting stage involves in all cases the formation of a solvent-separated ion pair[45,72]. Analogous features were manifested on comparing a more restricted set of data for t-BuCl and Ph_2CHCl: in proton-donating solvents Ph_2CHCl reacts faster by ~3 orders of magnitude than t-BuCl,[73] while in acetonitrile the rates are similar[74].

Thus the heterolysis of t-BuX proceeds via the formation of intermediate solvent-separated and contact ion pairs. The former predominate in proton-donating solvents, while the latter predominate in aprotic solvents. A contact ion pair is apparently formed in the gas phase[75,76]. In a few individual instances (in phenol and water) the reaction can proceed partly via a carbonium ion.

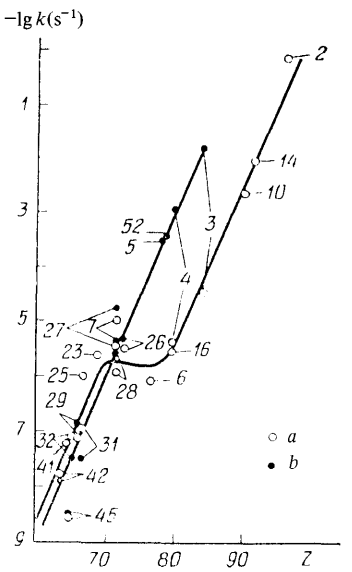
t-Butyl halides do not enter into a reaction via the S_N2 mechanism owing to the strong repulsion in the transition state between the nucleophile and the methyl groups[1,3,10,15]. In 1959 Winstein et al.[68] showed that the conclusion by Ingold[77] and other workers[78,79] according to which the substitution in t-BuCl(Br) in solution in acetone proceeds via the S_N2 mechanism must be treated merely as an unsuccessful hypothesis. However, when one of the methyl groups in t-BuX is substituted by a more electron-accepting group ($ArSO_2CH{=}CH{-}$) substitution via the S_N2 mechanism (more precisely via an S_N2 ion pair) at a tertiary carbon atom becomes possible[80]. Consequently the different reactivities of tertiary carbon in reactions involving the S_N1 and S_N2 mechanisms are due to both steric and electronic effects of the substituents.

The possibility of the operation of the $E2$ mechanism has been discussed[41,65,81,82]. The evidence against this reaction mechanism is that the yield of the olefin and the deuterium isotope effect in the solvolysis of t-BuCl are almost independent of the basicity of the mixed solvent[40], although in the presence of strong bases this reaction pathway is possible[59,83].

It is believed[84,85] that the smallness of the kinetic isotope effect and the deviation of the rate of heterolysis of t-BuCl in CF_3CH_2OH from the linear relation between $\lg k_{t\text{-}BuCl}$ and $\lg k_{1\text{-}AdBr}$ (where 1-AdBr is 1-adamantyl bromide) show that the elimination of HCl from the ion pair $t\text{-}Bu^+Cl^-$ is rate-limiting. However, comparison of the rates of heterolysis of t-BuCl, 1-AdCl, and 2-chloro-2-methyladamantane in various solvents, including fluorinated alcohols, shows[54,55] that all these substrates react via the same mechanism. This rules out the possibility of dehydrohalogenation as the rate-limiting stage.

According to Hammett[3], analysis of the kinetics of solvolysis of t-BuX is complicated by the reaction involving the internal return of the ion pair (with a rate constant k_{-1}). Harris[14] believes that the return reactions (k_{-1}, k_{-2}, and k_{-3}) are unimportant for t-BuX; elimination, dissociation of ion pairs, (k_2, k_3), or the interaction of the intermediates with the solvent predominate for these substrates. The absence of mixing of the oxygen in the solvolysis of t-BuOCAr[1,16] and
$$\text{t-BuO}\overset{\overset{\displaystyle{}^{18}O}{\|}}{C}\text{Ar}$$
2,4-dimethylhex-4-yl phthalate[86] is used as an argument against the occurrence of the internal ion pair return. However, it is believed[40] that, absence of the mixing of ^{18}O in t-alkyl derivatives can be caused by steric effects in the presence of which the reconversion takes place without mixing.

The occurrence of internal return is indicated by the formation of a sulphone on solvolysis of t-BuOSOAr.[87] The possibility of external return is indicated by the unimolecular exchange of the anion in t-BuX [26,32,64,65] and the salt effect based on the Law of Mass Action[62]. Analysis of the dependence of the heat capacities of activation on the composition of the medium (H_2O–EtOH) and on temperature led Blandamer et al.[88] to the conclusion that at ~20 °C the rates of internal return and of the elimination of HCl from $t\text{-}Bu^+Cl^-$ are approximately the same. Bentley and co-workers[54,55] and Harris et al.[85] believe that the observed deviations in weakly nucleophilic solvents such as CF_3CH_2OH and $(CF_3)_2CHOH$ are due to reactions involving the ion pair return and are not caused by the rate-limiting dehydrochlorination. As mentioned above, the proportions of the products following the addition of HCl to isobutene in CF_3CH_2OH clearly indicate the occurrence of the stage involving internal ion pair return[14,16,60].



Dependence of $\lg k_{t\text{-}BuBr}$ (*a*) and $\lg k_{Ph_2CHBr}$ (*b*) on Z (data from Table 1 and Refs. 70 and 71). The numbering of the solvents is the same as in Table 1; 52 = n-PrOH.

The influence of the solvent on the rate of reaction is attributed to its electrostatic and acid–base properties[2-5,20,22-89,90,91]. When the reaction is carried out in solution, it is always necessary to take into account the effect of non-specific solvation[4,20,23], although recently attempts have been made frequently to reduce the influence of the solvent on the kinetic parameters solely to its acid–base properties[22,90,92,93]. It is believed[94] that the high rate of solvolysis in water is caused by the presence of a small amount of OH groups not bound by a hydrogen bond and of unshared electron pairs (~6%).

The rate of heterolysis of t-BuX is known to depend strongly on the electron-accepting properties of the solvent[4,23]. This is indicated by the increase of the rate of reaction owing to the formation of hydrogen-bonded complexes with the departing group[1,4,5,15,95] and also by the catalysis by metal ions[5,96–99], which is described by an equation analogous to the Brønsted equation[5,100]. The great importance of electrophilic solvation in the heterolysis of t-BuX is indicated by the comparison of the rates of elimination of HBr from t-BuBr in a weakly polar ($\varepsilon = 15$) but electrophilic solvent such as SO_2 and in propylene carbonate, which is a strongly polar solvent ($\varepsilon = 70$). In the former case[101] at −15 °C we have $k = 5.2 \times 10^{-5}$ s^{-1}, while in the latter case[102] $k = 9.4 \times 10^{-7}$ s^{-1} (calculated from the temperature variation of k).

The question of the nucleophilic cooperation of the solvent in the heterolysis of t-BuX is still controversial[55,92,93,103]. On the basis of data for Ph_3CCl, Swain suggested in 1948 a push-pull character of the effect of the solvent on the heterolysis of t-BuCl.[104] Thornton[40] developed this hypothesis into the concept of a continuous spectrum of S_N1–S_N2 mechanisms. In 1970 Schleyer and co-workers[105] compared the rates of solvolysis of t-BuCl and 1-AdBr in various solvents and concluded on the basis of the observed deviations in a weakly nucleophilic medium ($CF_3CH_2OH + H_2O$) that the heterolysis of t-BuCl in other solvents proceeds with the nucleophilic cooperation of the sovlent. However, the same deviations are observed on comparing the rates of heterolysis of 1-AdBr and 1-AdOTos [106] and the rates of heterolysis of t-BuCl and 1-AdCl are poorly correlated with one another[15], although the correlation observed on comparing 1-AdBr and t-BuBr was on the whole satisfactory[54] and the deviations were the same as in the comparison of t-BuCl and 1-AdBr.

Other examples of the correlation between the rates of solvolysis of t-BuCl with the rates of solvolysis of various substrates can be found in the literature[15,107]; some of these lead to the conclusion that nucleophilic cooperation by the solvent takes place, while others indicated their absence. All this demonstrates the unreliability of the conclusions based on such comparisons. One of the causes may be the formation of different intermediates depending on the nature of the substrate and the solvent[108]. Thus it follows from a comparison of the rates of solvolysis[109] that the stability of the cations decreases in the sequence $Ph_3C^+ > t\text{-}Bu^+ > 1\text{-}Ad^+$, although it has been shown[110,111] that $1\text{-}Ad^+$ is more stable than $t\text{-}Bu^+$. The cause of the observed differences between the rates may consist in the fact that the rate of heterolysis of t-BuX is limited by the stage involving the formation of a contact ion pair, while in other instances more polar intermediates are produced[16,112,113]. However, to a first approximation, the rate of solvolysis reflects the stability of the cationic intermediate[35].

Evidence in support of the nucleophilic involvement of the solvent has been obtained in the case of DMF.[32,114] It has been shown[115] that the heterolysis of the bond at a tertiary carbon atom can proceed with the nucleophilic cooperation of a neighbouring group [the solvolysis of $PhSO-(CH_2)_nCR_2Cl$]. The conclusion that the cation formed in the solvolysis of t-BuBr undergoes nucleophilic solvation was based on the analysis of the dependence of $\Delta C_p^{\neq}$ on m (where $\Delta C_p^{\neq}$ is the heat capacity of activation and m is the sensitivity of the solvolysis to the influence of the solvent in the Grunwald–Winstein equation) for certain substrates in different media[116]. It is believed[32] that the higher value of $\Delta S^{\neq}$ in the heterolysis of t-BuBr in acetonitrile (amounting to −42 J mol^{-1} K^{-1}) [117] compared with that in $MeNO_2$ (−67 J mol^{-1} K^{-1}) [118] is due to the fact that the tendency towards nucleophilic solvation, of the charges separated in the transition state, by acetonitrile is smaller. Comparison of the nucleophilicity parameters of these solvents (see Table) shows that acetonitrile is more nucleophilic. In addition it has been shown[119,120] that $\Delta S^{\neq} = -84$ J mol^{-1} K^{-1} in acetonitrile. It is believed[14] that the heterolysis of t-alkyl substrates proceeds without the nucleophilic cooperation of the solvent. Fairly convincing evidence has been adduced[10] against the nucleophilic involvement of the solvent in the heterolysis of t-BuX. Indeed a solvent molecule can hardly attack the carbonium ion formed "from the rear" if even a charged nucleophile is incapable of it.

In 1972 Koppel and Palm[20] carried out a correlation analysis of the solvation effects in the heterolysis of t-BuCl and showed that the rate of reaction is independent of the nucleophilic properties of the medium. Later Fawcett and Krygowski[93] concluded that the basicity of the solvent influences the rate of heterolysis of t-BuCl—its influence on the rate constant is to the extent of ~20%. Other workers[22,92], who used the donor (DN) and acceptor (AN) numbers of the solvents, arrived at an analogous conclusion.

Bentley and Carter[121] recently summarised the available evidence in support of nucleophilic cooperation of the solvent in the heterolysis of t-BuX. They believe that this reaction proceeds via the mechanism involving an S_N2-intermediate (its rate is limited by the stage in which an ion pair is formed on treatment of the covalent substrate with a nucleophile[15]). The main evidence adduced by the above workers[121] reduces to the fact that in weakly nucleophilic solvents [acetic acid, formic acid, trifluoroacetic acid, CF_3CH_2OH, and $(CF_3)_2CHOH$] the rate of heterolysis of 1-AdCl(Br) is higher than would follow from the linear relation between $\lg k_{t\text{-BuX}}$ and $\lg k_{1\text{-AdX}}$ and that the rates of heterolysis of 1-AdX and t-BuX in these solvents are similar, while in a nucleophilic medium (80% ethanol) t-BuX reacts faster by ~3 orders of magnitude than 1-AdX. Bearing in mind that the $1\text{-}Ad^+$ cation is more stable in the gas phase than $t\text{-}Bu^+$,[110,111] the authors[121] conclude that the observed differences between the rates of reaction in 80% ethanol can be explained by the nucleophilic cooperation of the solvent in the heterolysis of t-BuX. The authors[121] ignore the fact that the weakly nucleophilic solvents which they enumerated are at the same time comparatively strong acids; the cause of the observed differences can therefore be the fact that the adamantyl substrates are more susceptible to electrophilic catalysis than the t-butyl substrates[15,16].

We may note that, when $\lg k_{1\text{-AdBr}}$ is plotted against $\lg k_{1\text{-AdCl}}$ on the basis of the values quoted by Bentley and Carter[121], deviations from linearity are also observed in the weakly nucleophilic (strongly electrophilic) medium owing to the increase of the rate of heterolysis of 1-AdCl. If one follows the reasoning of Bentley and Carter[121], one must conclude that the heterolysis of 1-AdBr proceeds with nucleophilic cooperation by the solvent, while the heterolysis of 1-AdCl takes place without such cooperation, which is absurd. As in the comparison of the rates of heterolysis of t-BuX and 1-AdX, here the differences between the reactivities of the substrate decrease with increase of the electrophilicity (or with decrease of the nucleophilicity) of the medium). From our point of view, the natural explanation is that the chlorides, forming more stable hydrogen-bonded complexes with proton-donating solvents than the bromides, are more sensitive to electrophilic catalysis. In addition, one must bear in mind that in the heterolysis of 1-AdX and t-BuX different intermediates can be formed in the rate-limiting stage and, even when the same intermediate is formed in both cases, for example, a solvent-separated ion pair, the energies of the solvation of the cation and anion by the internal ligand in $1\text{-}Ad^+|Solv|X^-$ and $t\text{-}Bu^+|Solv|X^-$ can vary greatly as a function of the nature of the solvent.

As a second argument in support of S_N2-substitution in t-BuX, Bentley and Carter[121] point to the formation, noted by Bunton and Nayak[122], of radioactive t-BuCl* in the solvolysis of t-BuCl in aqueous methanol (the authors erroneously state that aqueous acetone was used) in the presence of NaCl*. This example cannot serve as evidence in support of the S_N2 mechanism since in aqueous methanol there is a possibility of the formation of solvent-separated ion pairs and a carbonium ion, which leads to the exchange of the anion via the S_N1 mechanism involving the external return of the ion (k_{-3}) or the ion pair (k_{-2}).

Thus, the examination of the entire set of data, including the publications of recent years, shows that the question of the nucleophilic involvement of the solvent in the heterolysis of t-BuX still remains controversial.

In the interpretation of the solvent effects, one must bear in mind that the time required for t-BuX to pass from the initial to the transition state is usually shorter than the orientational relaxation time of the solvent molecules (the lifetime of the transition state is 10^{-13} s and the orientational relaxation time of the dipole is 10^{-10}–10^{-11} s).[23] Evidence has been presented[50] in support of the view that the maximum stabilisation of the transition state and the highest rate of the process are attained only under the conditions of equilibrium solvation of the transition state.

III. KINETIC PARAMETERS OF THE HETEROLYSIS OF t-BuX IN THE GAS PHASE AND IN INDIVIDUAL SOLVENTS

Table 1 presents the logarithms of the rate constants for the heterolysis of t-BuCl(Br, I) at 25 °C and the parameters of the solvents which we used for the correlation analysis. The heterolysis rate constants have been determined for all three alkyl halides in only 8 of the 50 solvents and in the gas phase; t-BuCl was investigated mainly in proton-donating solvents (21 out of 35), t-BuI in aprotic solvents (21 out of 23), and t-BuBr approximately to equal extents in both groups of solvents (9 out of 13). This restricts the scope of comparative analysis.

Table 2. The activation parameters of the heterolytic reactions of t-BuX.

Solvent	$\Delta H^{\neq}_{25}$, kJ mol^{-1}	$\Delta S^{\neq}_{25}$, J mol^{-1}K^{-1}	$\Delta G^{\neq}_{25}$, kJ mol^{-1}	Refs.
t-BuCl				
Gas phase	185.9	10.0	183.4	[123]
H_2O	97.1	51.1	81.6	[137]
MeOH	104.3	−13.0	107.6	[137]
EtOH	109.3	−13.4	113.5	[140]
n-BuOH	118.1	6.3	116.0	[127]
t-BuOH	110.5[b]	8.4[b]	108.0[b]	[129]
n-HexOH	120.2	6.7	118.1	[127]
n-OctOH	121.4	6.7	119.7	[127]
PhOH	69.5[c]	−100.9[c]	99.7	[92, 132]
HCO_2H	87.9	−7.1	90.0	[137]
CH_3CO_2H	108.0	−10.5	111.4	[137]
$PhNH_2$	79.1	−100.5	108.0	[136]
$HCONH_2$	93.8	−15.9	97.6	[137]
DMF	105.5	−56.1	122.3	[41]
Propylene carbonate	85.8	−115.1	120.2	[102]
$MeNO_2$	97.1	−75.4	119.3	[149]
MeCN	100.1	−74.9	122.3	[119]
Me_2CO	85.4	−153.7	127.7	[139]
t-BuCl	144.0[e]	−22.6[e]	150.7	[143]
$PhNO_2$	107.6[f]	−71.2[f]	128.5	[140]
n-Heptane	164.1	−1.3	164.5	[145]

Table 2 (contd.).

Solvent	$\Delta H^{\neq}_{25}$, kJ mol^{-1}	$\Delta S^{\neq}_{25}$, J mol^{-1}K^{-1}	$\Delta G^{\neq}_{25}$, kJ mol^{-1}	Refs.
t-BuBr				
Gas phase	170.0[a]	7.1[a]	169.1	[123]
H_2O	91.7	58.6	73.7	[126]
MeOH	98.0	−2.1	98.4	[126]
EtOH	103.0	−1.7	103.8	[126]
t-BuOH OH	97.6	−14.7	102.2	[129]
CH_3CO_2H	100.9	−8.0	103.4	[126]
EtCONHMe	93.8[d]	−38.5[d]	105.1	[41]
DMF	87.1	−59.9	105.1	[41]
N-Methylpyrrolidinone	92.5[g]	−47.7[g]	107.2	[65]
Propylene carbonate	84.6	−66.6	104.3	[102]
$MeNO_2$	83.7	−65.7	103.8	[118]
MeCN	81.6[h]	−83.7[h]	106.8	[119]
Me_2CO	81.6[i]	−119.3[i]	113.9	[139]
PhCN	90.0	−78.3	113.5	[141]
CH_2Cl_2	69.5	−149.5	114.3	[142]
Dichloroethane	77.0	−134.8	117.2	[142]
$(CO_2Et)_2$	62.4	−180.0	116.0	[144]
$PhNO_2$	85.0	−93.0	112.6	[141]
t-BuI				
Gas phase	154.9[a]	0.8[a]	154.5	[123]
CH_3OH	92.1	−9.6	95.5	[125]
Propylene carbonate	70.8	−84.6	95.9	[102]
MeCN	71.6	−86.7	97.6	[119]
Me_2CO	79.5	−77.0	102.6	[139]
$PhNO_2$	80.4	−81.2	104.7	[141]
PhCN	83.7	−68.3	103.8	[141]
$PhCF_3$	117.7	33.1	108.0	[141]
C_6H_6	75.4	−117.7	110.5	[141]
PhF	98.4	−40.6	110.5	[141]
PhCl	77.5	−97.6	110.5	[141]
PhBr	88.3	−75.4	111.0	[141]
PhI	78.3	−107.6	110.1	[141]
PhOMe	81.2	−94.6	109.3	[141]
$PhCH_3$	82.1	−104.3	113.0	[141]
CH_2Cl_2	72.9	−117.7	108.0	[142]
CH_2ClCH_2Cl	82.9	−85.4	108.4	[142]
CH_2BrCH_2Br	92.1	−71.6	113.5	[142]
Dioxan	49.8	−207.7	111.8	[144]
THF	83.3	−89.6	110.5	[144]
$(CO_2Et)_2$	57.8	−169.6	108.4	[144]
$PhCO_2Et$	72.4	−132.7	112.2	[144]
$MeCO_2Et$	71.6	−139.4	113.0	[144]
Other substrates				
Gas phase, t-BuF[j]	208.5[j]	14.2[j]	203.9	[150]
H_2O, t-BuF[k]	100.5	−32.2	110.1	[151]
Gas phase, t-BuOEt[l]	213.5	−28.1	219.4	[152]
CH_3CN, t-$BuONO_2$[m]	92.1	−35.6	102.6	[149]
MeCN, t-BuOTos[n]	79.5	−20.9	85.4	[153]
H_2O, t-BuOAc[o]	108.9	23.4	101.7	[154]
H_2O, t-BuOP(O)EtH[o]	91.7	−33.5	101.7	[155]
H_2O, t-BuOP(O)(OH)$_2^-$	97.6	−16.7	102.6	[156]
H_2O, t-$BuS^+Me_2I^-$[p]	108.4	−12.6	112.2	[157]

Remarks. [a]Calculated from the values of k at 230–680 °C; $\Delta H^{\neq} = 188.8$ kJ mol^{-1} and $\lg A = 19.93$ have been obtained by Hegtman et al.[158] for t-BuCl. [b]At 27 °C; $\Delta H^{\neq}$ and $\Delta S^{\neq}$ depend greatly on temperature; $\Delta H^{\neq}_{60°} = 19.7$ kJ mol^{-1} and $\Delta S^{\neq}_{60°} = -268.0$ J mol^{-1} K^{-1}. [c]Calculation from the values of k at 45°, 50°, and 55 °C. [d]Calculation from the values of k at 24.8°, 39.2° and 50.7 °C. [e]Calculation from the values of k at 100° and 120 °C [145] yields $\Delta H^{\neq} = 89.2$ kJ mol^{-1} and $\Delta S^{\neq} = -145.7$ J mol^{-1} K^{-1}. [f]Calculation from the values of k at 39°, 53°, and 70 °C.[140] [g]At 20°, 40°, and 60 °C; [HBr] ≅ 0.0275 M. [h]$\Delta H^{\neq} = 93.8$ kJ mol^{-1} and $\Delta S^{\neq} = -41.9$ J mol^{-1} K^{-1} are quoted by Hoffman[117]. [i]Calculation from the values of k at 20°, 40°, 44.4°, 50°, and 60 °C [68] yields $\Delta H^{\neq} = 78.7$ kJ mol^{-1} and $\Delta S^{\neq} = -126.4$ J mol^{-1} K^{-1}. [j]Calculation from the values of k at 315–370 °C; $\lg k^{25} = -22.9$. [k]$\lg k^{25} = -6.49$. [l]$\lg k^{25} = -25.6$. [m]$\lg k^{25} = -5.16$. [n]$\lg k^{25} = -2.20$. [o]$\lg k^{25} = -5.00$. [p]$\lg k^{25} = -6.71$.

Simple comparison of the rate constants shows that the sensitivity of t-BuX to changes in the nature of the solvent on passing from one proton-donating solvent to another (H_2O–MeOH) or from a proton-donating solvent to another solvent (MeOH–propylene carbonate) decreases in the sequence Cl > Br > I, which can be explained by the fact that in the series of departing groups indicated the capacity of the solvent for electrophilic cooperation in the heterolysis diminishes. Indeed the sensitivity of t-BuX to the change of the aprotic solvent depends comparatively little on the nature of the halogen.

The rate of heterolysis of t-BuX decreases in the leaving-group order (Table 2):

$$OTos > I > ONO_2 > Br > Cl > OAc \approx OPOEtH \approx OPO(OH)_2 > F > SMe_2I.$$

The differences between the rates diminish with increase of the acidity of the proton-donating solvent; for example, $\lg(k_{t\text{-BuBr}}/k_{t\text{-BuCl}})$ decreases monotonically from 1.6 to 1.0 in the series MeOH–H_2O–HOAc–HCO_2H (the increasing influence of the formation of hydrogen-bonded complexes abolishes the effect of the departing group). In the gas phase and in aprotic solvents the above ratio is higher ($\lg k^{Br}/k^{Cl} \cong 2.7$; $\lg k^{I}/k^{Cl} \cong 4.3$) and depends little on the nature of the solvent. In CH_2Cl_2 these quantities are lower (2.3 and 3.4 respectively)—here the influence of the formation of hydrogen-bonded complexes is also manifested[142].

Table 2 presents a compilation of the activation parameters for the heterolytic reactions of t-BuCl, t-BuBr, and t-BuI and presents certain data for the heterolysis of t-BuF, t-$BuONO_2$, t-BuOTos, t-BuOAc, t-BuOEt, t-BuOP(O)EtH, t-$BuOP(O)(OH)_2$, and t-$BuS^+Me_2I^-$.

Analysis of the relations between $\Delta H^{\neq}$ and $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$, and $\lg k^{25}$ and $\lg k^{50}$ for t-BuCl(Br, I) in various solvents[159] indicates the non-uniformity of the interaction[11] in the series considered, as shown by the failure of the isokinetic relation and the absence of the compensation effect. This may be due to the different degrees of charge separation in the transition state in various media, in agreement with the earlier conclusion that the rate-limiting stage is the formation of a contact ion pair in aprotic solvents and of the solvent-separated ion pair in proton-donating solvents.

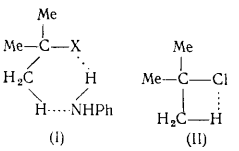
The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ vary marketdly as a function of the nature of the solvent—from 164.1 kJ mol^{-1} (n-heptane, t-BuCl) to 49.8 kJ mol^{-1} (dioxan, t-BuI) and from −207.7 kJ mol^{-1} (dioxan, t-BuI) to 58.6 kJ mol^{-1} K^{-1} (water, t-BuBr); therefore the conclusions that $\Delta S^{\neq} \geqslant 0$ [160,161] or that $\Delta H^{\neq}_{S_N1} > \Delta H^{\neq}_{S_N2}$ and $\Delta S^{\neq}_{S_N1} > \Delta S^{\neq}_{S_N2}$ [2,12,13] for reactions involving the S_N1 mechanism have little justification. The $\Delta S^{\neq}$ as a rule decreases in the series of solvents H_2O > proton-donating solvents > aprotic solvents; in the first case $\Delta S^{\neq} > 0$, in the second case $\Delta S^{\neq} \cong 0$, and in the third case $\Delta S^{\neq} < 0$. This can be explained by the fact that on formation of the transition state in water the effect of structure breaking in the solvent[162] predominates over the ordering of the latter as a result of the solvation of the ion pair produced; in other proton-donating solvents these effects are approximately identical, while in polar aprotic solvents the decrease of $\Delta S^{\neq}$ is due mainly to structure formation in the solvent around the ion pair formed.

The disruption of the structure of a proton-donating solvent with the aid of ultrasound increases the rate of solvolysis of t-BuCl.[103] The addition of small amounts of H_2O_2, ROH, tetrahydrofuran (THF), or acetonitrile also leads to the destabilisation of the water structure and hence to an increase of the rate of solvolysis of t-BuX.[163,164] The increase of the stability of the water structure on passing from H_2O to D_2O entails a decrease of the rate of solvolysis of t-BuCl ($k_{H_2O}/k_{D_2O} = 1.3$ was obtained at 25 °C [165]) with a simultaneous increase of $\Delta S^{\neq}$.[166] The negative value of $\Delta S^{\neq}$ for t-BuF in H_2O is associated with the formation of strong hydrogen bonds in the transition state, while $\Delta S^{\neq} \cong 0$ in n-heptane indicates an insignificant solvation of the transition state. Indeed, in the gas phase $\Delta S^{\neq}$ is also close to zero. $\Delta S^{\neq} = 33.1$ J mol^{-1} K^{-1} for t-BuI in $PhCF_3$ can be explained by the preferential solvation of the initial state as a result of the dipole–dipole interaction

$$(C^{\delta+}—F^{\delta-},\ C^{\delta+}—I^{\delta-}).$$

On formation of the transition state the dimensions of the $C^{\delta+}$–$I^{\delta-}$ dipole greatly increase, which leads to desolvation (disruption of the quadrupole).

The values $\Delta S^{\neq} \cong -80$ J mol^{-1} K^{-1} in certain proton-donating solvents (aniline, phenol) can be explained by the formation of a cyclic solvate complex of type (I) in the transition state[48,136]:



In aprotic solvents containing groups with a high dipole moment (CN, NO_2, CO), the formation of a quadrupole between the substrate and the solvent molecule is to be expected[3,4,141,167], which should reduce $\Delta S^{\neq}$ by ~80 J mol^{-1} K^{-1}; [12,120] the lower values of $\Delta S^{\neq}$ (from −125 to −210 J mol^{-1} K^{-1}) [dioxan, $(CO_2Et)_2$, CH_2Cl_2, RCO_2Et)] are apparently associated with the formation of complex cyclic associated species in the transition state[142,144]. This also applies to t-BuCl in propylene carbonate and acetone. The low value of $\Delta S^{\neq}$ in benzene is probably caused by the interaction of the substrate with the induced dipole of the C_6H_6 molecule[168].

In the gas phase and in non-polar aprotic solvents, $\Delta S^{\neq}$ is close to zero or has a low positive value. This conflicts with the hypothesis of the formation of a four-membered transition state of type (II) [6,18,48,49,142] in a medium of low polarity, since an appreciable decrease of $\Delta S^{\neq}$ is in fact to be expected precisely under the given conditions on formation of a cyclic transition state; this occurs, for example, on decomposition of t-BuOEt (Table 2). The increase of $\Delta S^{\neq}$ in acetonitrile in the sequence t-BuX < t-$BuONO_2$ < t-BuOTos can be explained by the decrease of the steric requirements in the dipolar solvation of the transition state, while the increase of $\Delta S^{\neq}$ in water in the sequence t-BuF < t-BuOAc < t-BuCl < t-BuBr is probably caused by the decrease of the solvation energy of the departing group.

It is noteworthy that $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can vary markedly with temperature; for example, in the solvolysis of t-BuCl in t-BuOH, $\Delta H^{\neq}$ decreases by ~84 kJ mol^{-1} and $\Delta S^{\neq}$ by ~290 J mol^{-1} K^{-1} on raising the temperature from 27° to 60 °C (Table 2).[129,169] In this case the heat capacity of activation is $\Delta C_p^{\neq} = -2760$ J mol^{-1} K^{-1}; in water $\Delta C_p^{\neq} = -347$ J mol^{-1} K^{-1}.[170] The values of $\Delta C_p^{\neq}$ ranging from −125 to −625 J mol^{-1} K^{-1} for S_N1 reactions are usually accounted for by the necessity for the reorganisation of the solvation shell when the substrate passes to the activated state[170,171] or more precisely by the temperature variation of the solvation of the anion formed[172,173]. Indeed $\Delta C_p^{\neq}$ can depend greatly not only on the solvent but also on the nature of the departing group ($\Delta C_p^{\neq} = -255$ J mol^{-1} K^{-1} for t-BuBr in t-BuOH [129]). $\Delta C_p^{\neq} < -650$ J mol^{-1} K^{-1} and its marked decrease on passing from t-BuBr to t-BuCl cannot be explained either by the influence of temperature on the solvation of the anion generated[173], or by the presence

of a stage involving ion pair return[165,174,175], or by large errors in the determination of the temperature variation of the rate constant[176]. The above effects are apparently associated with the structure of the solvent and its temperature variation[173,177]. This may be confirmed to some extent by the fact that in the hydrolysis of the compound RX the quantity $\Delta C_p^{\neq}$ in D_2O is always lower than in H_2O.[166] The significant role of the solvent structure is indicated by the fact that the rate of solvolysis of t-BuCl in the $(CF_3)_2CHOH-H_2O$ mixture passes through a minimum when the solvent composition corresponds to the dihydrate $(CF_3)_2CHOH.2H_2O$,[178] while the rate of hydrolysis of $PhCH_2Cl$ passes through a minimum at the temperature of the maximum density of water[179].

IV. SOLVATION EFFECTS

We carried out a correlation analysis of the influence of solvent parameters on $\lg k$ [71,180] on the basis of the equation

$$\lg k = a_0 + a_1 DN + a_2 AN + a_3\delta^2 \qquad (1)$$

and the Koppell–Palm equation[11,20] with inclusion of the Hildebrand parameter[6] δ^2:

$$\lg k = a_0 + a_1\frac{n^2-1}{n^2+2} + a_2\frac{\varepsilon-1}{2\varepsilon+1} + a_3\delta^2 + a_4 B + a_5 E\ , \qquad (2)$$

where DN is the donor number[21,90], AN the acceptor number[22,90], n the refractive index, ε the dielectric constant, B an empirical parameter of the basicity (nucleophilicity)[11,20], E empirical parameter of the electrophilicity calculated[11,20] from the Dimroth–Reichardt polarity parameter[91] E_T by the formula $E = E_T - 25.10 - 14.84f(\varepsilon) + 9.59f(n)$, and $\delta^2 = (\Delta H_M - RT)/V_M$ the Hildebrand parameter which characterises the energy of interaction of solvent molecules with one another; ΔH_M is the molar heat of evaporation and V_M is the molar volume. The solvent parameters are listed in Table 1. The Hildebrand parameter has been used in a number of studies for the interpretation of kinetic data[6,22,46,181], although it is frequently employed in the relatively unsuitable form of the solubility parameter δ.[6,46] For comparison with the data of Fawcett and Krygowski[93], we also carried out a calculation by Eqn.(2) with E replaced by E_T. In order to determine the influence of each parameter, the calculation was performed with successive inclusion of the parameters in accordance with the procedure of Chapman et al.[182] (the solvents for which the error exceeded the average error by a factor greater than or equal to 2.5 were rejected). The calculation was carried out on a Mir-2 computer.

The application of Eqn.(2) to t-BuCl in 28 solvents (solvents 2–9, 11, 13, 16–21, 23–31, 41, 45, 47) # yields the expression:

$$\lg k = -18.2 + 16.6f(n) + 7.06f(\varepsilon) + 4.77\delta^2 + 0.293E \quad (r=0.960,\ S=0.664).$$

When account is taken of B, we obtain $r = 0.961$. When the parameters δ^2, $f(n)$, $f(\varepsilon)$, and E are excluded, the values of r decrease respectively to 0.946, 0.945, 0.928, and 0.749. Thus the rate of hydrolysis of t-BuCl depends mainly on the electrophilicity of the solvent, to a lesser extent on its polarity, and depends little on the polarisability and self-association energy of the solvent. The nucleophilicity of the solvent does not influence the rate of reaction. These conclusions are consistent with the results of the calculations for t-BuCl by the Koppel–Palm equation[20,159].

In order to deduce the specific features of the solvation effects in proton-donating and aprotic solvents, we carried out calculations by Eqn.(2) separately for each group of solvents. In 15 proton-donating solvents (solvents 2–8, 11, 13, and 16–21), we obtained the equation

$$\lg k = -15.4 + 19.7f(n) + 5.10\delta^2 + 0.263E \quad (r=0.962,\ S=0.554).$$

When account is taken of B and $f(\varepsilon)$, we obtain $r = 0.964$; without taking into account δ^2, $f(n)$, and E, the values of r are respectively 0.934, 0.878, and 0.877. Thus in proton-donating solvents the rate of solvolysis of t-BuCl depends equally on the electrophilicity and polarisability of the solvent and to a lesser extent on its self-association energy; the basicity and polarity of the solvent do not affect the rate of reaction.

The rate of decomposition of t-BuCl in 13 aprotic solvents (solvents 23–31, 41, 45, 47, and 51) is described by the equation

$$\lg k = -20.8 + 14.1f(n) + 14.2f(\varepsilon) + 0.523E \quad (r=0.956,\ S=0.754).$$

When account is taken of B and δ^2, we obtain $r = 0.961$; when $f(n)$, $f(\varepsilon)$, and E are disregarded, the values of r are respectively 0.941, 0.743, and 0.856. Thus the ionisation of t-BuCl in aprotic solvents depends most on the polarity of the solvent, greatly on its electrophilicity, and depends only slightly on its polarisability.

When E is replaced by E_T in Eqn.(2),[20] we obtain the following equation for t-BuCl in 28 solvents (solvents 2–9, 11, 13, 14, 16, 17, 19, 21, 23–31, 41, 45, and 47):

$$\lg k = -21.5 + 3.67\delta^2 - 0.00351B + 0.289E_T \quad (r=0.960,\ S=0.697). \qquad (3)$$

Taking into account $f(n)$ and $f(\varepsilon)$, we have $r = 0.961$; when δ^2, B, and E_T are disregarded, the values of r are respectively ~0.952, 0.949, and 0.730. Consequently the rate of heterolysis of t-BuCl actually depends on E_T (the nucleophilicity actually decreases somewhat the rate of reaction in this case). Our results conflict with the conclusion[93] that the rate of heterolysis of t-BuCl increases with increase of both the electrophilicity (E_T) and basicity (DN) of solvents. We may note that Fawcett and Krygowski[93] used only five solvents ($r = 0.909$), while we used 28 solvents.

The application of Eqn.(1) to the description of the rate of heterolysis of t-BuCl in 15 solvents (solvents 2–4, 6, 16, 19, 23, 24, 27–29, 31, 41, 45, and 47) yields the expression

$$\lg k = -12.4 + 0.0917AN + 10.6\delta^2 \quad (r=0.980,\ S=0.606). \qquad (4)$$

When account is taken of DN, we have $r = 0.800$; when AN and δ^2 are disregarded, the values of r are 0.897 and 0.899 respectively. Thus the rate of heterolysis of t-BuCl depends equally on AN and δ^2. The basicity of the solvent does not affect the rate of reaction, which conflicts with the conclusions[22,92] that the rate of reaction increases appreciably with increase of DN.

Following the replacement of δ^2 by δ in Eqn.(1), the correlation becomes appreciably worse[180].

The application of Eqn.(2) to t-BuBr leads to the following relation in 14 solvents (solvents 2, 4, 14, 16, 23, 25–29, 31, 32, and 41):

$$\lg k = -8.00 + 10.3\delta^2 + 0.0883E \quad (r=0.972,\ S=0.481).$$

When account is taken of $f(n)$, $f(\varepsilon)$, and B, we have $r = 0.984$; when δ^2 and E are disregarded, the values of r are respectively 0.871 and 0.960. Consequently the rate of heterolysis of t-BuBr is determined fairly completely by δ^2; the electrophilicity of the solvent promotes the reaction to a slight extent, while the polarisability, polarity, and nucleophilicity of the solvent have no importance.

#Here and henceforth the solvents are numbered as in Table 1.

When E is replaced by E_T in Eqn.(2), we obtain the following expression for t-BuBr in 14 solvents (solvents 2–4, 16, 23, 25–29, 31, 32, 41, and 42):

$$\lg k = -11.8 + 9.68\delta^2 + 0.0954E_T \quad (r = 0.969,\ S = 0.502). \qquad (5)$$

When account is taken of f(n), f(ε), and B, we have $r = 0.981$. When δ^2 and E_T are disregarded, the values of r are 0.900 and 0.960. Thus the rate of heterolysis of t-BuBr depends mainly on δ^2; allowance for E_T improves the correlation slightly.

The application of Eqn.(1) to t-BuBr yields the following relation for 12 points (solvents 2, 4, 16, 23, 26–29, 31, 32, 41):

$$\lg k = -8.53 + 0.0137DN + 0.0252AN + 11.7\delta^2 \quad (r = 0.976,\ S = 0.488). \qquad (6)$$

The exclusion of AN or DN has comparatively little influence on the correlation coefficient (r = 0.975 and 0.964 respectively), while the exclusion of δ^2 lowers r to 0.770. Thus the rate of heterolysis of t-BuBr depends virtually only on δ^2. The correlation of the rates taking into account only DN and AN (or E_T and B) leads to poor results.

The application of Eqn.(2) to t-BuI in 19 solvents (solvents 2, 3, 26, 28, 29, 31, 32, 34–42, 45, 46, and 49) yields the expression

$$\lg k = -9.69 + 6.32f(\varepsilon) + 11.8\delta^2 \quad (r = 0.965,\ S = 0.491).$$

When account is taken of f(n), B, and E, we have $r = 0.975$; when f(ε) is disregarded, r = 0.952. Consequently the rate of heterolysis of t-BuI depends mainly on δ^2.

Following the replacement of E by E_T, we obtain the following equation for the same 19 solvents:

$$\lg k = -12.5 + 5.72\delta^2 + 0.147E_T \quad (r = 0.973,\ S = 0.437).$$

Taking into account f(n), f(ε), and B, we obtain $r = 0.976$; when δ^2 and E_T are disregarded, the values of r are 0.953 and 0.952. Thus the rate of heterolysis of t-BuI is equally well correlated with both δ^2 and E_T. The nucleophilicity of the solvent does not affect the rate of reaction.

Application of Eqn.(1) to t-BuI in 11 solvents (solvents 2, 3, 26, 29, 31, 32, 34, 41, 45, and 46) leads to the relation

$$\lg k = -7.38 + 0.0455AN + 8.77\delta^2 \quad (r = 0.966,\ S = 0.668). \qquad (7)$$

Our correlation analysis showed that the rate of heterolysis of t-BuX is independent of the nucleophilic properties of the medium. In all cases the contribution of the parameters B or DN was close to or equal to zero with the exception of Eqn.(3), where B actually reduces slightly the rate of reaction. Consequently we conclude that the heterolysis of t-BuX proceeds without the nucleophilic cooperation by the solvent. This agrees with the conclusions of Koppel and Palm[20] and also Kulik[159] and conflicts with the conclusions of the authors of a number of studies[15,22,32,40,54,55,85,92–94,104,105,114,116,118], who believe that the formation of the transition state requires nucleophilic attack by the solvent. Our Eqns.(4), (6), and (7) showed that the conclusions[22,90,92–94] concerning the influence of the acid–base properties of the solvent on the rate of heterolysis of t-BuX are only half justified—only as regards the acid properties of the solvent.

Recently Abraham et al.[183] correlated the values of lg k for t-BuCl(Br, I) in 15 specially selected solvents (solvents 2–4, 7, 16, 23–26, 28, 29, 45, 47, 50, and 51) in terms of the Koppel–Palm equation and the equation

$$\lg k = a_0 + a_1\pi^* + a_2\alpha + a_3\beta, \qquad (8)$$

where π^* is the dipolarity parameter and α and β are the parameters of the electrophilicity and nucleophilicity of the solvents respectively[183]. In the former case the rate of reaction is described by a three-parameter equation including f(ε), f(n), and E with correlation coefficients of 0.975 (t-BuCl), 0.963 (t-BuBr), 0.934 (t-BuI), while in the latter case it is described by a two-parameter equation (the parameters π^* and α) with $r \cong 0.995$. This provided the authors[183] with grounds for the conclusion that Eqn.(8) describes the solvent effect better than the Koppel–Palm equation. Naturally a two-parameter equation is always better than a three-parameter equation, since the latter suffers from an uncertainty in its derivation[185,186], but the conclusions of Abraham et al.[183] provide only for the set of solvents indicated from which aromatic and organic polychloro-solvents have been excluded. Furthermore, out of the 45 values of lg K quoted by Abraham et al.[183], 14 had been calculated and four (t-BuBr in isopropyl alcohol, t-butyl alcohol, diethyl ether, and dioxan) had been taken from an unknown source—the values indicated are missing from Refs.6, 18, and 128 to which Abraham et al. refer[183]. Recently published data[129] on the solvolysis of t-BuBr in t-BuOH show that the value quoted by Abraham et al.[183] ($\lg k_1^{25} = -6.50$) is lower by 1.5 orders of magnitude than the experimental value (Table 1). It has been shown[159] that the correlation of the lg k for t-BuCl(Br, I) carried out for the entire set of solvents leads to better results. Consequently the set of solvents employed by Abraham et al.[183] on the one hand improved the correlation in terms of Eqn.(10) and on the other impaired the correlation in terms of the Koppel–Palm equation. In essence, the data obtained by Eqn.(10) agree well with the results of the correlation in terms of the Koppel–Palm equation, since it has been shown recently[187] that the parameter π^* is correlated with f(ε) and f(n). The main conclusion reduces in both cases to the rejection of the nucleophilic involvement of the solvent.

Nucleophilic attack by the solvent "from the rear" can actually hinder the unimolecular heterolytic reaction. Indeed the nucleophilic solvation of the carbonium ion generated leads to the stabilisation of the intermediates formed and hence can retard their subsequent migration along the reaction coordinate. It has been shown[32] that the nucleophilic involvement of a DMF molecule in the heterolysis of 2-bromo-2-methylpentane leads to the establishment of the dead-end equilibrium

$$\mathrm{DMF} \cdot \mathrm{R^+Br^-} \underset{-\mathrm{DMF}}{\overset{+\mathrm{DMF}}{\rightleftharpoons}} \underset{\mathrm{RBr}}{\mathrm{R^+Br^-}} \rightleftarrows \mathrm{R^+ \mid Solv \mid Br^-} \rightarrow \text{products}.$$

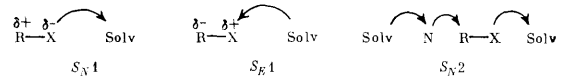
Consequently the intuitive hypothesis of Bentley and Schleyer[15] that the substrate should "make use" of the nucleophilic cooperation by the solvent does not occur on the main reaction pathway if it obtains at all.

In contrast to the nucleophilicity factor, other solvent parameters influence the rate of heterolysis of t-BuX and, depending on the nature of the leaving group or the set of solvents, any one of them can predominate.

The rate of heterolysis of t-BuCl in the entire set of proton-donating and aprotic solvents is determined mainly by the electrophilicity. The solvent polarity and polarisability promote the reaction to an appreciable extent. Calculation by the Koppel–Palm equation[129] shows that the solvent electrophilicity is also of decisive importance for t-BuBr and t-BuI.

It is possible to put forward the following picture of the mechanism of the unimolecular heterolysis of t-BuX: as a result of the action of the internal nucleophile (the t-butyl group), an electron is transferred to the departing group and this is sufficient for the rapid subsequent elimination of HX in the gas phase. In the condensed phase the reaction is to a large extent promoted by the delocalisation of the charge of the anion generated over the solvent molecule, i.e. by the electrophilic cooperation in the heterolysis. The positive charge generated does not require the nucleophilic cooperation by the solvent since it is sufficiently delocalised over the three methyl groups. Furthermore, the action of

the nucleophile is hindered by the pronounced steric hindrance. For reactions via the S_E1 mechanism, one can outline the opposite picture: in this case the nucleophilic cooperation in the heterolysis becomes decisive[188]. Reactions of the S_N2 type require both the nucleophilic and electrophilic cooperation by the solvent[93,189]. Hence follows a simple generalisation concerning the role of the solvent in substitution reactions:



S_N1 S_E1 S_N2

Analysis carried out separately in proton-donating and aprotic solvents[180] makes it possible to define and specify in greater detail the mechanism of the heterolysis of t-BuCl.

In proton-donating solvents the rate of reaction depends equally on the electrophilicity and polarisability of the solvent and is described by the two-parameter equation

$$\lg k = -(15.7\pm1.4) + (19.3\pm2.0)f(n) + (0.383\pm0.026)E \quad (r=0.934).$$

In aprotic solvents the decisive factor is the polarity and to a lesser extent the electrophilicity:

$$\lg k = -(17.7\pm1.7) + (15.5\pm1.4)f(\varepsilon) + (0.441\pm0.051)E \quad (r=0.941).$$

The dependence of the rate of heterolysis of t-BuCl in proton-donating solvents on the electrophilicity and polarisability factors can be explained by the fact that, as a result of the formation of hydrogen-bonded complexes by the anion generated, the negative charge is strongly delocalised over the solvent molecule, which leads to the formation of a readily polarisable transition state. In an aprotic medium the dependence of the rate of reaction mainly on the solvent polarity can be accounted for by the fact that in this instance the heterolysis occurs as a result of the dipole–dipole interaction of the t-BuCl molecules with solvent molecules[3,4,23,120,141]. If this is so, the rate of reaction should increase with increase of the dipole moment of the solvent. Indeed a satisfactory correlation has been observed between ε and μ (for solvents 23, 24, 26–32, 35–39, 41, 42, 45–47):

$$\mu = -13.0 + 13.4\varepsilon \quad (r=0.969,\ S=1.30).$$

The solvation of the anion generated should play a smaller role in this instance, which is in fact observed.

The differences between the rates of heterolysis of t-BuX in proton-donating and aprotic solvents are associated to some extent with the fact that in the former case a solvent-separated ion pair is formed in the rate-limiting stage, while in the latter case a contact ion pair is produced. It has been shown[44] that the formation of a solvent-separated ion pair depends much more on the formation of hydrogen-bonded complexes than the formation of a contact ion pair.

If *AN* is employed as the electrophilicity parmeter, the rate of heterolysis of t-BuCl is described satisfactorily by the two-parameter Eqn.(4), which also includes δ^2.

In contrast to t-BuCl, the rate of heterolysis of t-BuBr and t-BuI depends mainly on the self-association energy of the solvent, which is determined by the cohesive energy density and polarity of the solvent. We have

$$\lg k = -(8.06\pm0.28) + (13.9\pm1.2)\delta^2 \quad (r=0.963)$$

for t-BuBr and

$$\lg k = -(7.11\pm0.32) + (12.8\pm1.5)\delta^2 \quad (r=0.952)$$

for t-BuI.

One should note that δ^2 is an independent parameter. Indeed δ^2 is hardly correlated with the four parameters of Eqn.(2)—r = 0.72 for 41 solvents (solvents 2–9, 11, 13, 16–21, 23–32, 34–42, 45–47, 50, and 51). The maximum correlation coefficient among the one-parameter relations is observed for the δ^2–E relation (r = 0.70); allowance for the polarity parameter increases r to 0.72, while nucleophilicity and polarisability do not affect r. In proton-donating solvents (17 solvents) the multiple correlation coefficient is 0.83, while in aprotic solvents (24 solvents) it is 0.40.

The influence of the factor δ^2 on the rate of heterolysis of t-BuX can be explained by the fact that the residence time of the substrate in the solvent cage (10^{-8}–10^{-11} s) [23] and hence the probability of its ionisation increase with increase of the cohesion energy of the solvent. The migration of t-BuX relative to the solvent molecules leads to the dissipation of the energy required for the attainment of the transition state. If the influence of δ^2 is reduced solely to the energy required for the formation of the cage in the solvent, as is usually done[6,22,46], then it becomes incomprehensible why δ^2 should affect the rate of reaction if the process proceeds in the solution already formed. At the same time it is difficult to achieve a clear-cut interpretation of the dependence of the influence of δ^2 on the nature of the leaving group, since a different set of solvents has been used for each substrate.

In conformity with the rule of Richardson and Soper[190], the increase of the rate of heterolysis of t-BuBr with increase of the cohesion of the solvent shows that the products of the above reactions, or more correctly the transition state, have a greater cohesion than the initial reactants. The observed difference for t-BuCl can be hardly explained by the fact that in this case the cohesions of the reactants and reaction products, or more correctly $[t\text{-BuCl}]^{\neq}$, become equalised either due to the increase of the cohesion of t-BuCl or as a result of the decrease of the cohesion of the transition state. The explanation should apparently be sought in an increase of order in the solution[24] on passing from t-BuBr to t-BuCl. This conclusion is in good agreement with the latest interpretation of the low values of $\Delta C_p^{\neq}$ in S_N1 reactions[173], based on the concept that the solvent structure influences the solvation of the anion generated.

It is believed[129] that the marked decrease of $\Delta C_p^{\neq}$ in t-BuOH on passing from t-BuBr to t-BuCl is associated with the fact that the molecules of t-BuCl can enter freely into structural cavities or into the middle of the polymeric associated solvent species, while the molecules of t-BuBr are incapable of this. Cohesion therefore has apparently little influence on the heterolysis of t-BuCl, while a change in the solvent structure can lead to intense thermodynamic and kinetic effects[129,162,178]. It has been shown[191] that the stability of the solvation sphere around t-BuX depends on the nature of the halogen.

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Thus, the correlation analysis of the influence of solvent parameters shows that the rate of heterolysis of t-butyl halides depends mainly on the electrophilicity of the solvent and increases with its self-association energy. In all cases the heterolysis of t-BuX proceeds without the nucleophilic cooperation by the solvent.

In conclusion we may note that t-butyl halides are relatively unsuitable as standards for the comparative analysis of the influence of the solvent on solvolytic and other heterolytic reactions. Non-uniformity of the mechanism is characteristic of these substrates: a contact ion pair is formed in the rate-limiting stage in aprotic solvents, while a solvate-separated ion pair is formed in proton-donating solvents; in isolated instances (H_2O, phenol) carbonium ions are formed. Diphenylmethyl halides are more promising standards for the analysis of solvation effects.

During the preparation of the manuscript for the press, the paper of Swain et al.[192] was published and in it a correlation analysis has been carried out for 77 reactions in 61 solvents using the solvent electrophilicity (A) and nucleophilicity (B) parameters. The authors conclude that all the solvolytic reactions (26 systems) require both the nucleophilic and electrophilic cooperation of the solvent and that the influence of the nucleophilicity increases in the sequence Ph_2CHCl < t-BuCl < MeBr < 1-AdBr < t-BuBr. The series which they present[192] conflicts with modern ideas[14-16], according to which there should be no nucleophilic cooperation in 1-AdBr and such cooperation should be a maximum in MeBr. The reason for this discrepancy is that the parameters A and B of the solvents were calculated from the entire set of data on the basis of critical conditions arbitrarily selected by the authors[192]: $A = B = 1$ in water, $A = B = 0$ in hexane, and $A = 0$ in hexamethylphosphoramide and $B = 0$ in CF_3COOH. The parameters A and B obtained for other solvents as a result of the calculation[192] conflict with widely familiar experimental data. Thus, according to Swain et al.[192], acetic acid is less nucleophilic than formic acid and is less electrophilic than water. The lack of validity of the conclusions of Swain et al. [192] is associated also with the fact that they employed only an insignificant proportion of the experimental data. For example, out of the 35 known values of $\lg k$ for the heterolysis of t-BuCl in individual solvents only 6 were employed, while in the case of t-BuBr only 4 out of 21 were employed.

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Kiev Polytechnic Institute

Translated from *Uspekhi Khimii*, 53, 971-1013 (1984) U.D.C. 542.91+547.235+547.284

Advances in the Chemistry of β-Aminoketones

G.A.Gevorgyan, A.G.Agababyan, and O.L.Mndzhoyan

Data on the aminomethylation reaction (the Mannich reaction) for the period 1970-1980 are examined and a systematic account is given. The synthesis of β-aminoketones from various ketones (dialkyl ketones, alkyl aryl ketones, heterocyclic alkyl ketones, and cyclic ketones, as well as diketones) is discussed.
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I. INTRODUCTION

The interest in β-aminoketones (Mannich bases) has been stimulated recently by the following factors: (a) β-aminoketones are intermediates in the synthesis of α,β-unsaturated ketones, β-aminoalcohols, and heterocyclic compounds; (b) β-aminoketones are potentially biologically active compounds.

The main method of synthesis of β-aminoketones is based on the aminomethylation of ketones. The extensive literature on the aminomethylation reaction, called the Mannich reaction, has been systematically represented throughout in review articles[1-13], and monographs[14,15]. A review[16] is devoted to advances in the study of the Mannich reaction during the period 1960–1970.

In our own review article[17], we considered the aminomethylation reaction using α-aminoacids as the amino-components.

It is known that β-aminoacids possess a broad spectrum of biological activity. Many of them have found applications in medical practice. Thus the hydrochlorides of 4-(n-propoxy)- and 4-(n-butoxy)-β-piperidinopropiophenones (falicaine and dyclonine) as well as the hydrochloride of 4-(n-propoxy)-β-hexamethyleneiminopropiophenone (hexacaine) are used in medical practice as local anaesthetics[18-21], the hydrochloride of 4-methyl-α-methyl-β-piperidinopropiophenone (mydocalm) is used as an anticonvulsant[22], and the hydrochloride of 6-[β-(3-phenylpyrrolidino)propionyl]-1,4-benzodioxan (pyrroxan) is an α-adrenoblocking agent[23,24].

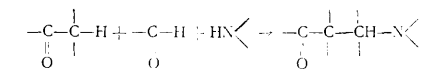
Furthermore, antibacterial[25-29], anti-inflammatory[30,31], antitumour[26,32-37], analgesic[37,38], psychotropic[39] and other properties[40-47] have been discovered in a large number of β-aminoketones.

The present review is devoted to the available literature data on the aminomethylation reactions of various ketones accumulated during 1970–1980 (and for diketones also up to 1970).

For clarity and to ensure brevity of exposition, we thought it useful to quote the biological activities of β-aminoketones in a separate column in the Tables.

II. AMINOMETHYLATION OF KETONES

One of the convenient methods of synthesis of β-aminoketones is the Mannich reaction, which consists of the condensation of a ketone containing at least one hydrogen atom in the α-position with an aldehyde (usually formaldehyde) and an amine:

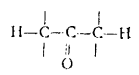


Numerous communications have been devoted to the study of the mechanism of this reaction[1,6-8,10,38,48].

1. Dialkyl Ketones

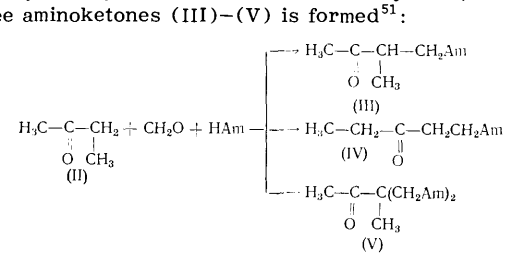
A number of studies have been made of the aminomethylation of asymmetric dialkyl ketones[49-63]. Despite the fact that the Mannich reaction has been studied for a long time, the problem of selectivity for asymmetric ketones has still not been fully solved. Some data[49] are now recognised as erroneous.

There are mobile hydrogen atoms in the α- and α'-positions in the molecules of dialkyl ketones of type (I), which suggests different modes of aminomethylation:



(I)

When ethyl methyl ketone (II) is aminomethylated, a mixture of three aminoketones (III)–(V) is formed[51]:

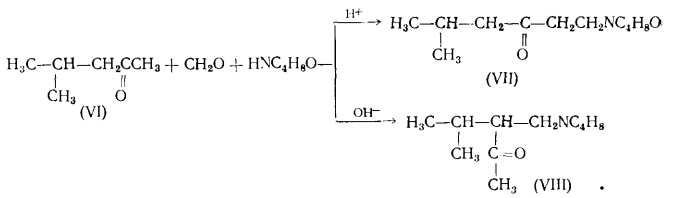


Am = $N(C_2H_5)_2$, NC_5H_{10}.

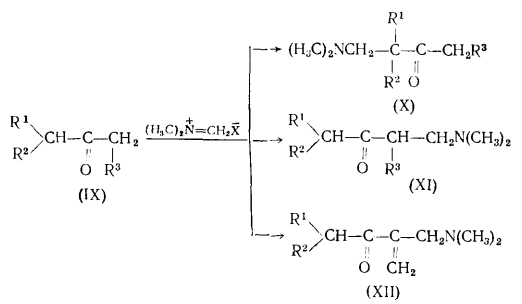
It has been shown that, with decrease of the pH of the medium, the yields increase: on heating ethyl methyl ketone, paraformaldehyde, and diethylamine in ethanol at pH 8–9 for 6 h, the overall yield of the mixture of aminoketones is 28.6%, while at pH 1 it is 43%. The formation of compound (IV) has been demonstrated by specific synthesis and also mass-spectrometrically[52].

The relation between the yields of the final products and the pH of the medium has also been considered[53].

The aminomethylation of 4-methyl-2-pentanone (VI) in ethanol in an acid medium leads to a mixture of 1-morpholino-5-methylhexanone (VII) and 1-morpholino-2-isopropyl-3-butanone (VIII) (in proportions of 69:31) with an overall yield of 81%, while in a basic medium a mixture of compounds (VII) and (VIII) is obtained with the latter predominating [(VII):(VIII) = 8:92]; the overall yield is 43%:



It has now become possible to direct aminomethylation to a particular α-carbon atom in an asymmetric ketone using immonium salts as the reagents. Thus the aminomethylation of the ketone (IX) [54–57] using the immonium salt $(CH_3)_2\overset{+}{N}=CH_2X^-$ (0.05 M, X = CF_3CO_2 or ClO_4) in trifluoroacetic acid at 72 °C leads to selective attack on the more substituted α-carbon atom with formation of compound (X):[56]



$R^1 = R^3 = H, CH_3$; $R^2 = CH_3, C_2H_5, n\text{-}C_4H_9$

$R^1 + R^2 = (CH_2)_n$, $n = 3–5$.

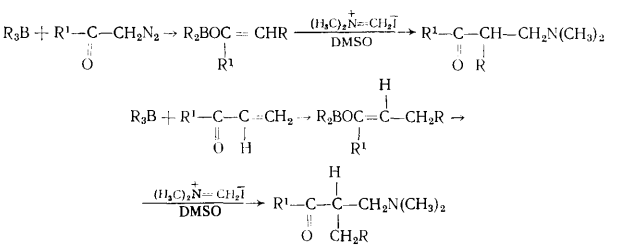
Table 1. The regioselective synthesis of the β-aminoketones (X) and (XI) from asymmetric ketones $RCOCH_3$ and immonium salts[55].

Immonium salt	R	Overall yield, %	(X):(XI)
Solvent F_3C-COOH			
$(CH_3)_2\overset{+}{N}=CH_2CF_3COO^-$	$C_6H_5CH_2$	95	85:15
ditto	CH_3CH_2	85	80:20
»	$(CH_3)_2CH$	90	85:15
»	cyclopentyl	90	95:5
»	cyclohexyl	70	69:31
Solvent CH_3CN			
$(C_3H_7)_2\overset{+}{N}=CH_2ClO_4^-$	cyclopentyl	80	0:100
ditto	$(CH_3)_2CH$	95	0:100
»	cyclohexyl	90	0:100

On increase of the concentration of the immonium ion to 2 M, the reaction product is compound (XI), which is formed, according to the authors, as a result of the isomerisation of the aminoketone (X).† In acetonitrile at 72 °C and in the presence of a 2 M concentration of the immonium ion, the reaction product is compound (XI), whose formation is accompanied by that of the aminoketone (XII), which contains the vinyl group. The sterically hindered dipropyl(methylene)ammonium salt reacts specifically with the methyl group in alkyl methyl ketones in acetonitrile (Table 1).

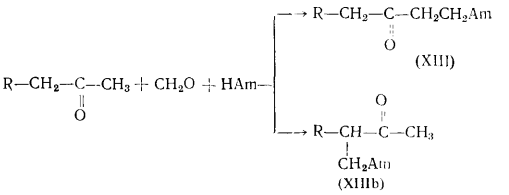
From the experimental data, the authors conclude that the regioselectivity is greatly influenced by the size of the group at the nitrogen atom, the solvent, the concentration of the immonium salts, and the counterion.

Enol borinates also react regiospecifically with dimethyl(methylene)ammonium iodide in dimethyl sulphoxide (DMSO).[54] The reaction constitutes an effective method of synthesis of Mannich bases from α-diazoketones or α,β-unsaturated ketones and aldehydes:



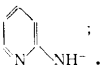
$R = C_2H_5, C_6H_{13}, C_7H_{15}$; $R^1 = C_6H_5$ $(CH_3)_2CH$.

Despite the possibility of aminomethylation at both methylene groups of the substituted acetone molecule[58–63], the products of aminomethylation at the methyl group have been characterised[58] [compound (XIIIa)], while other workers[59–61] characterised the products of aminomethylation at the methylene group [compound (XIIIb)]:

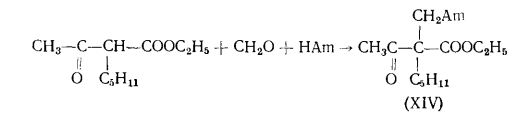


(a) $R = CH_2CH_2COOC_2H_5$, CH_2CH_2CN, $CH_2CH{=}C(Cl){-}CH_3$, $CH_2CH_2C_6H_4OCH_3$-*m*;

$CH_2CH_2{-}C(C_7H_4{-}OH\text{-}o)_2CH_3$; Am = $N(C_2H_5)_2$, NC_5H_{10}, $N(C_3H_7)_2$

(b) $R = C_6H_5$,  ; Am = $N(CH_3)_2$, $N(C_2H_5)_2$ NC_4H_8O

Optically active Mannich bases (XIV) have been obtained in 36–50% yield by the reaction of (+)-ethyl 2-methylbutylacetoacetate with paraformaldehyde and secondary amines[62]:



Am = $N(CH_3)_2$, $N(C_2H_5)_2$, $N(C_3H_7)_2$, $N(n\text{-}C_5H_{11})_2$, NC_5H_{10}, NC_4H_8O, $N(CH_2CH_2OH)_2$.

The above justifies the conclusion that, regardless of the pH of the medium, the aminomethylation of asymmetric dialkyl ketones leads to the formation of the α- and α′-aminomethyl derivatives and that in an acid medium the reaction involves

†In our view, the direct formation of compound (XI) cannot be excluded.

preferentially the less substituted α-carbon atom, while in an alkaline medium it involves the more substituted α-carbon atom. It has been suggested that the observed relation between the regioselectivity of the aminomethylation and the reaction conditions reflects the change in the relative rates of the enolisation and addition stages.

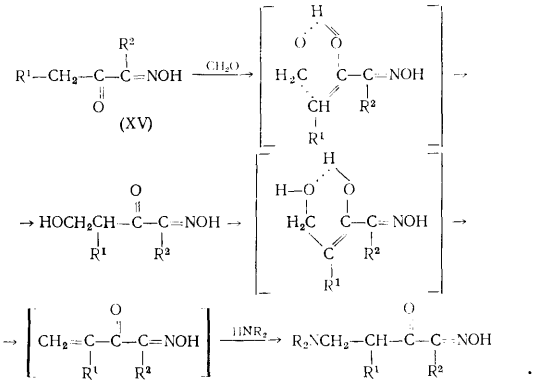
2. Isonitrosoketones

A number of studies have been made of the aminomethylation of α-isonitrosoketones[64-67]. It has been shown that the products of the aminomethylation of α-isonitrosoketones (XV) are mono-, di-, and tri-substituted derivatives (Table 2).

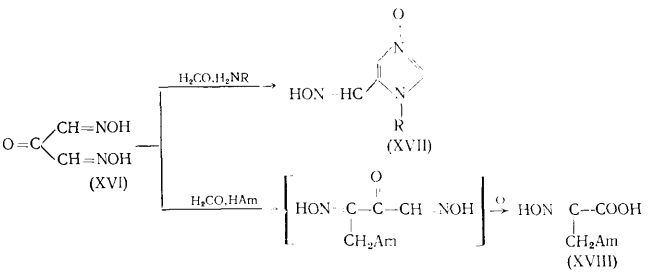
Table 2. The Mannich reaction involving substituted isonitrosoketones.

Initial ketone	Aminomethylation product	Yield, %	Refs.
$CH_3CH_2-C(=O)-C(=NOH)-CH_3$	$CH_3-CH(CH_2Am)-C(=O)-C(=N-OH)-CH_3$; Am = $N(CH_3)_2$, NC_4H_8, NC_5H_{10}	47—75	[64]
$CH_3-C(=O)-C(=NOH)-R^1$; R^1 = CH_3, C_6H_5, $COOC_2H_5$	$AmCH_2-CH(AmCH_2)-C(=O)-C(=NOH)-R^1$; Am = $N(CH_3)_2$, $N(C_2H_5)_2$, NC_4H_8, NC_4H_8O, NC_5H_{10}	31—90	[64]
$CH_3-C(=O)-CH(-NOH)$	$AmCH_2-CH(AmCH_2)-C(=O)-CH=NOH$; Am = $N(C_2H_5)_2$, NC_4H_8O, NC_5H_{10}	26—70	[65]
$C_5H_{10}NCH_2-CH(C_5H_{10}NCH_2)-C(=O)-CH=NOH$	$C_5H_{10}NCH_2-CH(C_5H_{10}NCH_2)-C(=O)-C(=NOH)-CH_2Am$; Am = $N(C_2H_5)_2$, NC_5H_{10}	35, 51	[65]

Hahn and Bartnik[64] proposed a probable reaction mechanism consisting of the following stages: (1) condensation of the formaldehyde with the CH acid component in which the amine behaves as a basic catalyst; (2) dehydration of the hydroxymethyl derivative formed; (3) nucleophilic addition of the amine to the double bond facilitated by the vicinity of the carbonyl group.

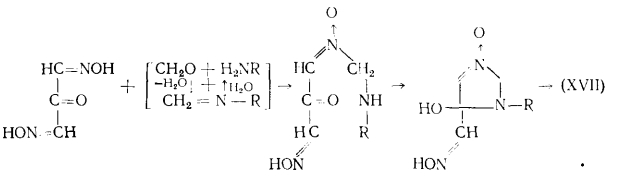


The mode of reaction of di-isonitrosoacetone (XVI) with formaldehyde and primary and secondary amines has been investigated. The reaction products are respectively derivatives of 5-(hydroxyiminomethyl)imidazole 3-*N*-oxide (XVII) and the oxime of aminopyruvic acid (XVIII):[67]



R = CH_3, C_2H_5, C_6H_{11}, $C_6H_5CH_2$, *p*-$CH_3OC_6H_4$, *p*-$C_2H_5OC_6H_4$
Am = NC_4H_8O, NC_5H_{10}.

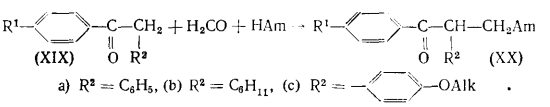
The authors explain the formation of compound (XVII) in the following way:



This is consistent with the data obtained by Lettau[68-72] for the condensation of isonitrosoketones with aldehydes and primary amines.

3. Alkyl Aryl Ketones

In order to investigate the problem of structure–reactivity relation, a large group of β-aminoketones (XX) have been synthesised by the Mannich reaction from substituted benzyl phenyl and cyclohexylmethyl phenyl ketones (XIX) (Table 3):[38,73-80]



a) $R^2 = C_6H_5$, (b) $R^2 = C_6H_{11}$, (c) R^2 = —OAlk.

It is known that the course of the Mannich reaction and the yields of products are significantly influenced by the pH of the medium[3,81]. The results of studies in recent years fully confirm this hypothesis[38,51,73-77]. Thus the yield does not exceed 28% in the condensation of the ketone (XIXa), paraformaldehyde, and pyrrolidine in an acid medium (pH 1–2) on heating for 30 h. On the other hand, in a

basic medium (pH 8–9) heating in the course of 4 h ensures a 70–90% yield of the aminoketone (XX):

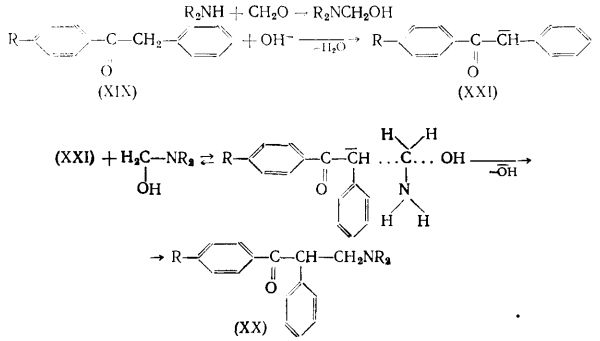
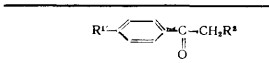
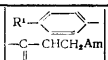
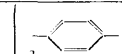


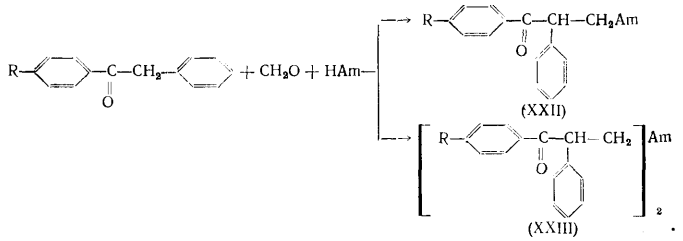
Table 3. Aminomethylation of benzyl phenyl and cyclohexylmethyl phenyl ketones.

			Yield, %	Biological activity	Refs.
R^1	R^2	Am			
H, HO, n-alkoxy-(C_1–C_7), iso-C_3H_7O, iso-$C_5H_{11}O$	C_6H_5	NC_5H_{10}	38–92	analgesic, anaesthetic	[73]
H, HO, n-alkoxy-(C_1–C_5), iso-$C_5H_{11}O$	C_6H_5	NC_4H_8O	46–89	—	[73]
H, HO n-alkoxy-(C_1–C_7), iso-C_3H_7O, iso-$C_5H_{11}O$	C_6H_5	NC_4H_8	28–91	ana.' analgesic	[74]
H	 R^3 = H, HO, n-alkoxy-(C_1–C_5), iso-C_3H_7O, iso-C_4H_9O, iso-$C_5H_{11}O$	NC_4H_8	32–62	ditto	[75]
H, n-alkoxy-(C_1–C_5)	C_6H_5	NC_6H_{12}	61–75	anti-inflammatory, antipyretic	[76]
H, HO, F, C_4H_9O, iso-C_3H_7O		NC_5H_{10}, NC_6H_{12}, HN—$CH(CH_3)_2$	43–91	ditto	[77]
H, n-alkoxy-(C_1–C_5), iso-C_3H_7O, iso-$C_5H_{11}O$	C_6H_5	$HNCH_3$, HNC_4H_9	47–80	loss of analgesic activity	[78]

In all probability the reaction proceeds via the S_N2 mechanism[38]. Presumably, with increase of the pH of the medium, the concentration of the carbanion (XXI) increases, which tends to increase the rate of reaction.

The opposite relation is observed in the aminomethylation of the ketones (XIXb).[77] Thus, when a reaction mixture consisting of equimolar amounts of cyclohexylmethyl phenyl ketone, paraformaldehyde, and hexamethyleneimine is heated for 15 h at pH 1.0 in dioxan, the yield is 83%, while at pH 7.0–8.0 it does not exceed 25–30%. In this case the reaction apparently proceeds via the electrophilic substitution mechanism (S_E).

When primary amines are used, the disubstituted derivative (XXIII) is formed together with the monosubstituted products (XXII):[75]



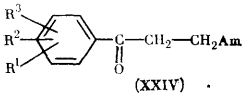
It is known that the biological activity of β-aminoketones is significantly influenced by the presence and position of an alkoxy-group in the benzene ring, the structure of the amino-group, and also the substituent in the α-position[18].

Pharmacological studies of the salts of the aminoketones (XXa, Am = NC_5H_{10}) showed that the methoxy- and ethoxy-derivatives completely lack a surface-anaesthetic activity. An increase of the length of the alkoxy-group to four carbon atoms results in the appearance of a moderate activity, which weakens as the length of the hydrocarbon chain is increased further to six atoms[45]. The hypotensive activity of these compounds increases with increase of the length of the alkoxy-group from methoxy- to pentoxy, after which it falls. The replacement of piperidine by pyrrolidine in the molecule of compounds (XXa) results in the appearance of both terminal and conductor anaesthesia. Some of them approach dicain as regards their anaesthetic activity and morphine as regards their analgesic activity[73].

The anti-inflammatory activity of the aminoketones (XX) has been investigated as a function of their capacity to arrest the haemolysis of rat erythrocytes. It has been shown that *in vitro* they all suppress the haemolysis of erythrocytes at a concentration of 10^{-3}–10^{-4} M and, after an increase in the length of the chain of the alkoxy-group, at 10^{-5}–10^{-9} M.[31]

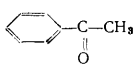
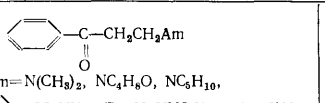
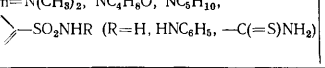
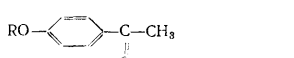
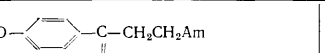
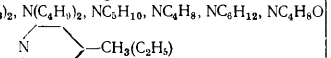
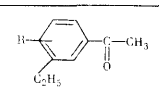
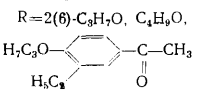
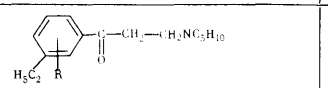
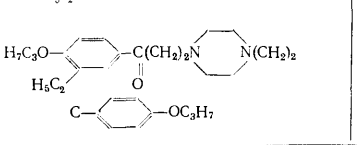
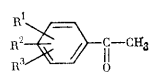
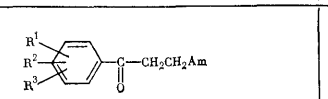
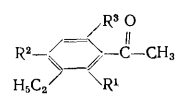
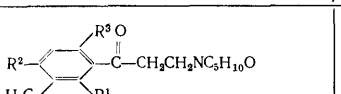
A change in the position of the alkoxy-group, as in compound (XXc, Am = pyrrolidine), and also the replacement of the cyclic amine by a primary amine (methylamine, butylamine) lead to the loss of analgesic activity[75,78]. The replacement of the phenyl group in the α-position by the cyclohexyl group, as in compound (XXb), is not reflected in the anti-inflammatory activity of the compounds, but some of them acquire antipyretic properties[77].

In order to investigate the relation between the chemical structure and biochemical activity, Schrotter and co-workers also synthesised a large group of β-aminoketones (XXIV) (Table 4):[82–87]



Piperidino-derivatives are the most active among the aminoketones (XXIV, R^1 = H, R^2 = 4-alkoxy-, R^3 = C_2H_5) and the intensity of the anaesthesia increases up to $R^2 = n\text{-}C_3H_7O$, remains constant up to $R^2 = n\text{-}C_6H_{13}O$, and then falls[83]. On the other hand, the maximum duration of the activity of the compound has been noted for the *n*-heptoxy-derivative. Compounds with iso-groups are inferior to the *n*-alkoxy-derivatives both as regards the intensity of the anaesthesia and the duration of the activity. It has been noted that, when the methyl or ethyl group is introduced into the 4-position of the piperidine residue, the strength and duration of the activity increase. The replacement of the 4-alkoxy-group in aminoketones (XXIV) by an alkoxy-group

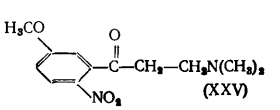
Table 4. Aminomethylation of acetophenones.

Initial ketone	Aminomethylation product	Yield, %	Biological activity	Refs.
	 Am=$N(CH_3)_2$, NC_4H_8O, NC_5H_{10}, HN– 	31—88	—	[88—90, 111]
 R=CH_3CO, C_4H_9CO, n-alkyl-(C_1—C_{10}), iso-C_3H_7, iso-C_4H_9, iso-C_5H_{11}, $C_4H_9O(CH_2)_2$, $C_5H_{11}O(CH_2)_2$, $C_6H_{13}O(CH_2)_2$, $C_2H_5O(CH_2)_4$, $C_3H_7O(CH_2)_4$, $C_4H_9O(CH_2)_4$	 Am=$N(CH_3)_2$, $N(C_4H_9)_2$, NC_5H_{10}, NC_4H_8, NC_6H_{12}, NC_4H_8O 	29—63	local anaesthetic, bacteriostatic	[82, 87]
 R=2(6)-C_3H_7O, C_4H_9O, 	 	41—63	ditto	[83—85, 94]
 R^1=Cl, Br, NO_2, iso-C_3H_7, OH; R^2=H, HO, CH_3, n-alkoxy-(C_1—C_6), $C_2H_5O(CH_2)_4O$, $C_3H_7O(CH_2)_4O$, $C_4H_9O(CH_2)_4O$; R^3=H, CH_3, CH_3O, Br, NO_2	 Am=$N(CH_3)_2$, $N(C_2H_5)_2$, $N(C_4H_9)_2$, NC_4H_8, NC_4H_8O, NC_5H_{10}, NC_6H_{12}	55—89	local anaesthetic	[86, 87, 98, 99, 112]
 R^1=C_3H_7, C_4H_9, H; R^2=H, C_3H_7, C_4H_9; R^3=H, C_3H_7, C_4H_9		*	ditto	[87]

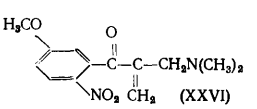
*The yields are given in grams.

[R^2 = 4-Alko-$(CH_2)_nO$; n = 2, 4] made it possible to obtain substances with the same activity but a greater duration of the latter[84]. Antiparasitic and antibacterial properties have been found in some aminoketones of the (XXIV) series[85,87].

The aminomethylation of substituted acetophenones has also been studied[43,88—116] (Tables 4—6). It has been shown that, when 5-methoxy-2-nitroacetophenone reacts with formaldehyde and dimethylamine hydrochloride in 1-butanol, β-dimethylaminomethyl-5-methoxy-2-nitropropiophenone (XXV) is formed[95,96]:

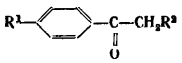

(XXV)

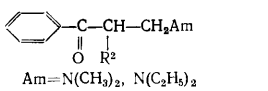
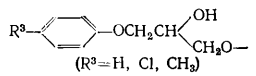
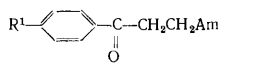
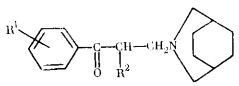
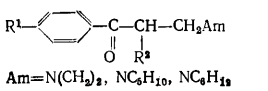
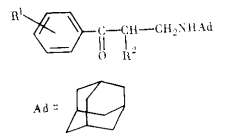
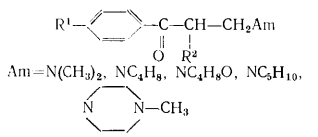
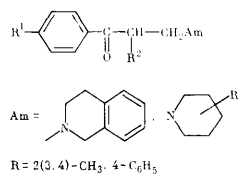
Subsequently, Back established that the aminomethylation of 2-nitro- and 2-ethoxycarbonyl-aminoacetophenones leads to the formation of 2-nitro- and 2-ethoxycarbonylamino-α-dimethylaminomethylacrylophenones (XXVI) in addition to the expected propiophenone derivatives[92,94]:


(XXVI)

The authors explained the formation of compound (XXVI) by the fact that, under the conditions of the Mannich reaction,

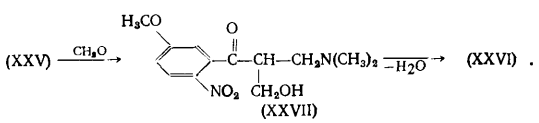
Table 5. Aminomethylation of α-substituted acetophenones.



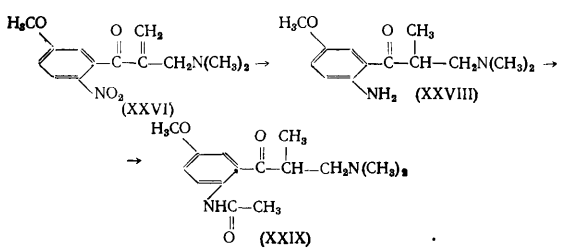
R^1	R^2	Reaction product	Yield, %	Biological activity	Refs
H	H, CH_3, C_6H_5	 Am=$N(CH_3)_2$, $N(C_2H_5)_2$	54—89	antimicrobial	[30]
Phenoxy-, substituted phenoxy-,  (R^3=H, Cl, CH_3)	H	 Am=$N(C_2H_5)_2$, $N(C_4H_9)_2$, NC_4H_8O, NC_5H_{10}	*	local anaesthetic	[100]
4-F, 4-Cl, 4-Br, 2(4)-benzyloxy-, 4-fluoro-benzyloxy-, 2,2-dimethylaminomethoxy-	H, CH_3, C_2H_5, C_3H_7		42—72	anticough	[101]
Hal, NO_2, iso-C_3H_7	H, CH_3, C_2H_5	 Am=$N(CH_3)_2$, NC_5H_{10}, NC_6H_{12}	*	hypotensive	[91, 102]
H, NO_2, Hal, OH	H, lower alkyl		20—40	antimicrobial	[103, 104]
H, CH_3, HO, F, F_3C, C_4H_9, NO_2, CH_3, C_2H_5, CH_3SO, CH_3SO_2	H, CH_3, C_3H_7, C_4H_9		20—76	stimulators of central nervous system	[106]
H, F	—		55—85	ditto	[40, 106]

*The yields are given in grams.

the *C*-hydroxymethyl compound (XXVII) is formed from compound (XXV) and its dehydration leads to compound (XXVI):

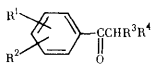


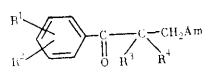
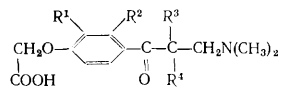
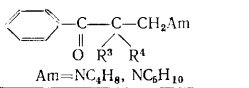
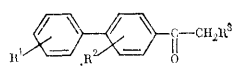
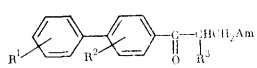
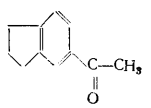
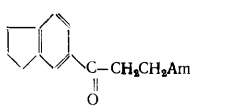
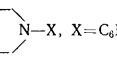
This has been confirmed by both physicochemical analytical methods and by various reactions of compound (XXVI).[92,94] Thus catalytic hydrogenation of compound (XXVI) and acetylation of the reduction product (XXVIII) lead to the formation of 2-acetamido-5-methoxy-α-methyl-β-dimethylaminopropiophenone (XXIX):



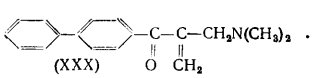
The formation of an acrylophenone derivative has been described also by Mann et al.[97] in relation to compound (XXX) as an example:

Table 6. Aminomethylation of substituted acetophenones.



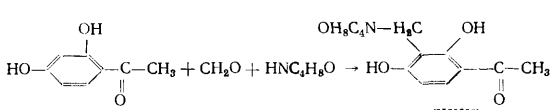
R^1, R^2	R^3, R^4	Reaction product	Yield, %	Biological activity	Refs.
Cl, CH_3, CH_3O, C_2H_5O	H, CH_3	 Am = NC_5H_{10}; NC_4H_8O	42—59	stimulators of central nervous system	[40]
H, Cl	H, CH_3, C_2H_5		22—93	diuretic	[43]
H, CH_3	H, CH_3, OCH_3	 Am=NC_4H_8, NC_5H_{10}	62—91	—	[110]
 R^1=H, Cl, NO_2, CH_3O; R^2=H, NO_2, CH_3; R^3=H, CH_3, C_6H_5		 Am = $N(CH_3)_2$, NC_5H_{10}	9—81	—	[97]
		 Am=NC_5H_{10}, HN—  ,  N—X, X=C_6H_5, *o*-(Cl, F, CH_3, CH_3O)C_6H_4, *m*-ClC_6H_4, *p*-(Cl, F)C_6H_4, CH_3, CH_2CH_2OH, $COOC_2H_5$, $CH_2C_6H_5$, 	•	sedative	[108]

*The yields are given in grams.

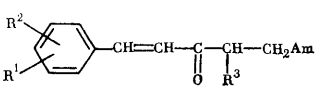

(XXX)

3,4,5-Trisubstituted acetophenones containing nitro-groups in the 3- and 5-positions are aminomethylated with difficulty (with a yield of 8—12%).[98]

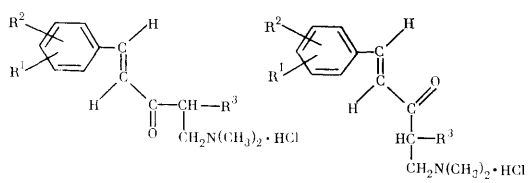
In the case of resacetophenone, the aminomethyl group enters the ring of compound (XXXI):[109]


(XXXI)

The aminoketones (XXXII) have been obtained by the condensation of substituted styryl ketones, paraformaldehyde, and amine hydrochlorides[26,34,36,60,107,117—128] (Table 7):


(XXXII)

According to infrared spectroscopic data, 4-dimethylaminomethyl-1-phenyl-1-ionen-3-ones (XXXII, $R^3 = C_5H_{11}$) exist in the *S-cis*- and *S-trans*-forms[118]:

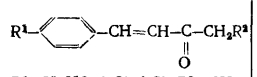
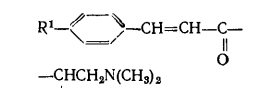
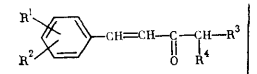
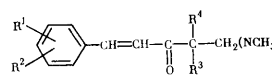
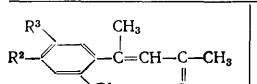
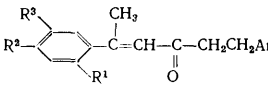
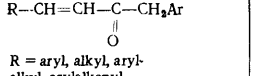
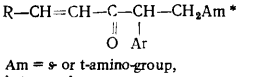
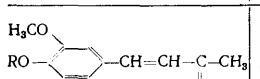
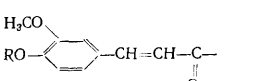
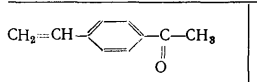
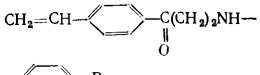

S-trans-(XXXII) *S-cis*-(XXXII)

Compounds (XXXII) possess various biological properties[26,34,36,60,107,120,122,123]. In particular, many hydrochlorides of derivatives of 5-dimethylamino-1-substituted phenylpent-1-en-3-ones [XXXII, R^1 = H or 2(3)-Cl; R^2 = H or 4(6)-Cl; $R^3 = (CH_2)_4CH_3$] exhibit pronounced cytotoxic properties[34,36,122].

Their antimitochondrial properties have been investigated[120,122]. It has been shown that their hydrochlorides manifest a high inhibiting activity, while the methiodides lack these properties. The antimitochondrial properties of the products of the deamination of the aminoketones (XXXII)

have also been studied and it has been shown that the unsaturated ketones are inactive in this respect[120].

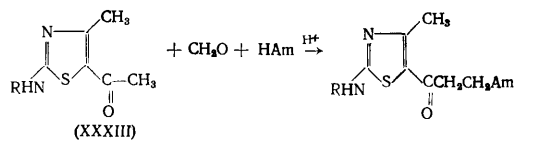
Table 7. Aminomethylation of styryl ketones.

Initial ketone	Aminomethylation product	Yield, %	Refs.
 R^1=H, HO, 2-Cl, 4-Cl, R^2=CH_3, n-C_5H_{11}		37—43	[26, 36, 120]
 R^1=H, 2-(3,4-)Cl, $N(CH_3)_2$; R^2=H, 4(6)Cl; R^3=H, n-C_5H_{11}; R^4=H, CH_3	 R^1=R^2=H; R^3=n-C_5H_{11}; R^4=CH_3	29—56	[36, 107, 118—123]
 R^1=H, CH_3; R^2=CH_3O, C_2H_5O; R^3=H, iso-C_3H_7	 Am=$N(CH_3)_2$, $N(C_2H_5)_2$, NC_4H_8, NC_4H_8O, NC_5H_{10}	43—50	[124, 125]
 R = aryl, alkyl, arylalkyl, arylalkenyl Ar = aryl with various substituents	 Am = s- or t-amino-group, heterocycle	**	[126]
 R=H, Ac		**	[127]
	 R=H, OH, CH_3, CH_3O, COOH, NO_2	24—62	[128]

*Possess antimicrobial and antimitotic activity.
**The yields are given in grams.

4. Heterocyclic Methyl Ketones

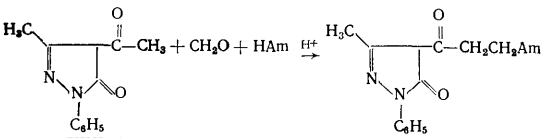
A number of studies have been made on the aminomethylation of heterocyclic methyl ketones[41,101,129—134]. It has been shown[130] that 2-substituted 5-acetyl-4-methylthiazoles (XXXIII) can be aminomethylated in concentrated hydrochloric acid or in a 2:1 acetic acid–dioxan mixture with a yield of 40–90%. The aminomethylation in ethanol, acetic acid, and dimethylformamide was unsuccessful:



(XXXIII)

R = H, $CH_3C(=O)$—, $C_6H_5C(=O)$—, m-$NO_2C_6H_4C(=O)$—, $ClCH_2C(=O)$—, Cl_3CH—$C(=O)$—, CH_3CH=CH—; Am = $N(CH_3)_2$, $N(C_2H_5)_2$, $N(iso\text{-}C_3H_7)_2$, NC_4H_8O, NC_5H_{10}

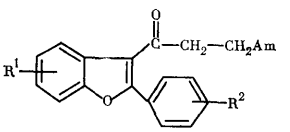
The aminoketones (XXXV) have been obtained in 60% yield by the aminomethylation of 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one (XXXIV) in ethanol in the presence of hydrochloric acid[131]:



(XXXIV) (XXXV)

Am = $N(C_2H_5)_2$, $N(C_6H_5)_2$, NC_4H_8O

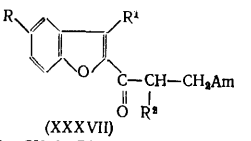
A method of synthesis of pharmacologically active aminomethyl derivatives of 3-acetylbenzofuran (XXXVI) has been patented[132]:



(XXXVI)

R^1 = H, a halogen, or lower alkyls: R^2 = H, a halogen, lower alkyls, or an alkoxy-group; Am = lower alkylamines, pyrrolidine, morpholine, piperidine, hexamethyleneimine, piperazine, or *N*-methylpiperazine.

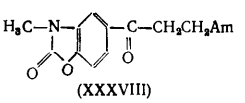
The aminoketones (XXXVII) have been synthesised by the condensation of substituted 2-acetylbenzofurans with formaldehyde and amines[134]:



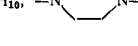
(XXXVII)

R = Cl, Br, CH_3O; R^1 = H, CH_3; R^2 = H, CH_3, C_2H_5; Am = $N(CH_3)_2$, $N(C_2H_5)_2$, NC_5H_{11}

β-Aminoketones of the benzoxazolinone series (XXXVIII), which exhibit an analgesic activity, have been obtained in 60–80% yield[41]:

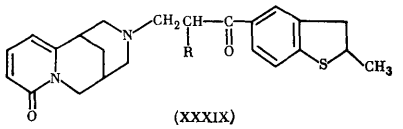


(XXXVIII)

Am = $N(CH_3)_2$, NC_4H_8O, NC_5H_{10}, 

Aminoketones derived from cytisine (XXXIX), whose cholinolytic activity exceeds that of cytisine itself, have

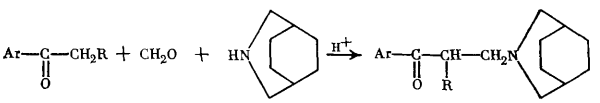
been obtained from substituted acetylthioindanones[133]:



(XXXIX)

R = H, CH_3 .

The aminoketones (XL), obtained by the interaction of substituted acetophenones or propiophenones with paraformaldehyde and the hydrochloride of 3-azabicyclo[3.2.2]-nonane in ethanol with added hydrochloric acid, possess an anticough activity[101]:



(XL)

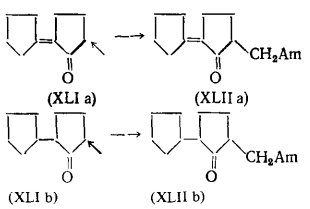
Ar = 3-pyridyl, 2-thienyl, 3-indolyl, or 1-(*N*-methyl-4-piperidinyl)-5-methyl-4-pyrazolyl; R = H or CH_3.

The aminomethylation of certain acetyl derivatives of steroids has been described[135–137].

5. Cyclic Ketones

A large number of publications have been devoted to the aminomethylation of cycloalkanones and their various derivatives[30,56,138–164], on the one hand, and heterocyclic ketones[167–204], on the other. Table 8 lists the substituted cyclopentanones and the corresponding Mannich bases.

Roth and Thassler showed that the aminomethylation of 2-cyclopentylidene and 2-cyclopentyl-cyclopentanones (XLI, a and b) in isopropyl alcohol results in the formation of the aminoketones (XLII, a and b) as the sole products[138]:



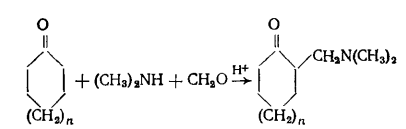
(XLI a) (XLII a)

(XLI b) (XLII b)

Am = $N(CH_3)_2$, NC_4H_8, NC_4H_8O, NC_5H_{10}, NHC_6H_{11}, $NHCH_2C_6H_5$.

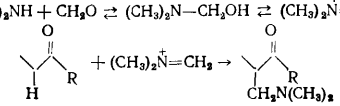
Table 9 lists the cyclohexanone derivatives and their aminomethylation products.

The aminomethylation of cyclohexanone and cyclopentanone involving the direct use of an immonium ion[143,144] generated in the reaction mixture has been studied:



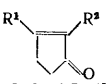
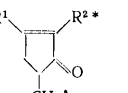
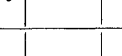
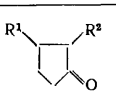
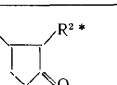
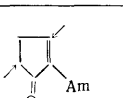
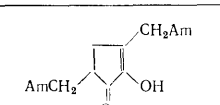
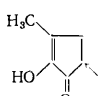
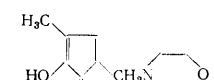
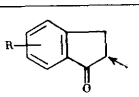
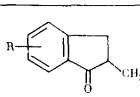
$n = 0, 1$

$$(CH_3)_2NH + CH_2O \rightleftarrows (CH_3)_2N{-}CH_2OH \rightleftarrows (CH_3)_2\overset{+}{N}{=}CH_2 \qquad (1)$$



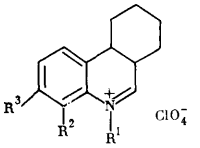
According to the authors, this method has the following advantages: (1) the concentration of the immonium ion is higher than that resulting from equilibrium (1) and the reaction is thus faster; (2) lower temperatures can be used; (3) an aprotic medium can be employed.

Table 8. Aminomethylation of cyclopentenones and cyclopentanones.

Initial ketone	Aminomethylation product	Yield, %	Refs.
 R^1=CH_3, C_6H_5, 4-FC_6H_4, $C_6H_5CH_2$, $CH_2CO_2C_2H_5$, *N,N*-diethylacetamido, acetylmorpholino-	 Am=$N(C_2H_5)_2$, NC_4H_8O, NC_4H_8, HNC_3H_7, HNC_6H_5, 	**	[30]
 R^1=CH_3, C_6H_5; R^2= alkyl (C_1—C_8)	 Am=$N(CH_3)_2$, HNC_4H_9, NC_4H_8O, NC_5H_{10}	**	[30]
	 Am=NC_4H_8, NC_4H_8O, NC_5H_{10}	61—73	[139]
		34.0	[140]
 R = CH_3, C_2H_5, iso-C_3H_7, Cl, Br, CH_3O	 Am=$N(CH_3)_2$, NC_4H_8, NC_5H_{10}, NC_4H_8O	60—75	[151]

*Exhibits analgesic and anti-inflammatory activity.
**The yields are given in grams.

The condensation of cyclohexanone with paraformaldehyde and secondary amines in the presence of an inorganic acid in 1-butanol leads to quaternary substituted tetrahydrophenanthridinium salts (XLIII):[145,146]

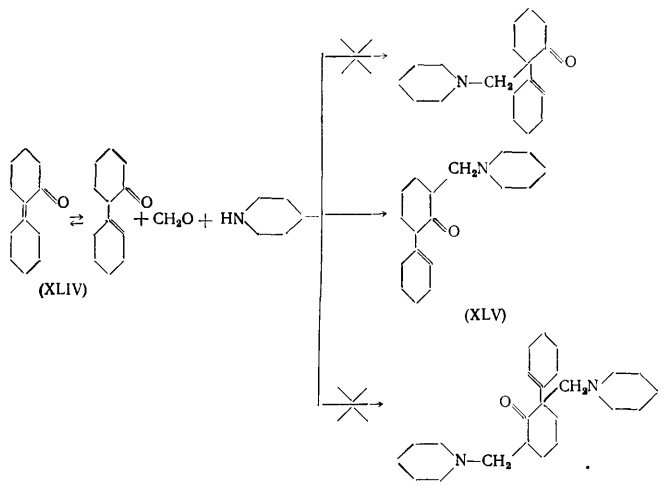


(XLIII)

R^1 = CH_3, C_2H_5, C_6H_5, $C_6H_5CH_2$; R^2 = R^3 = H; R^2 + R^3 = C_6H_5 .

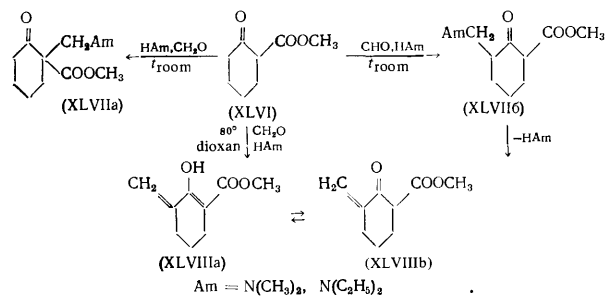
Although the aminomethylation of the 2-(cyclohex-1-enyl)-cyclohexanone (XLIV) molecule is possible in both the 2- and 6-position, the authors[147] showed that in benzene the only

product is the aminoketone (XLV):



(XLIV) (XLV)

Depending on the temperature and the duration of heating, the aminomethylation of 2-methoxycarbonylcyclohexanone (XLVI) proceeds via two different pathways[148]:

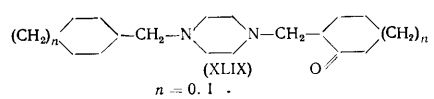


(XLVIIa) (XLVI) (XLVIIб) (XLVIIIa) (XLVIIIb)

Am = $N(CH_3)_2$, $N(C_2H_5)_2$

The above scheme shows that, at room temperature in dioxan, a mixture of compounds (XLVIIa) and (XLVIIb) in proportions of 55 : 45 is formed, while at 80 °C in dioxan compound (XLVIIIa), which is the enolic form of the deamination product of the Mannich base (XLVIIIb), is produced.

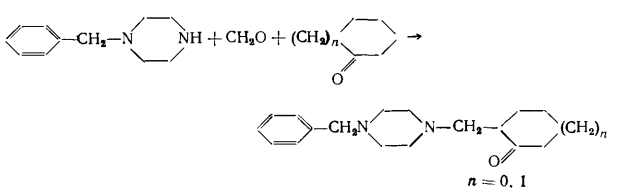
The synthesis of symmetrical Mannich bisbases (XLIX) has been studied[149]:



(XLIX)

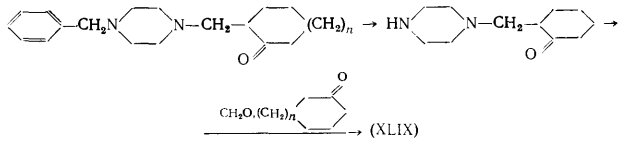
$n = 0, 1$.

Data have also been published on the synthesis of asymmetric Mannich bisbases. Having first protected one of the nitrogen atoms in the piperazine molecule by a benzyl group, the authors obtained a monosubstituted product:



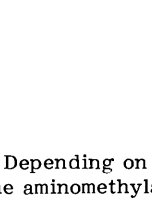
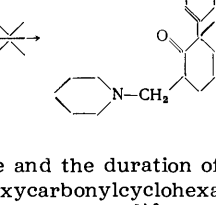
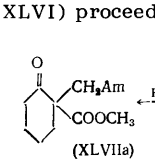
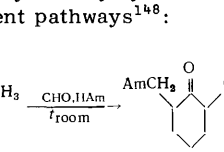
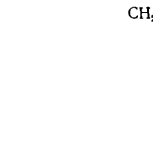
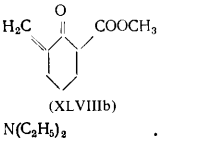
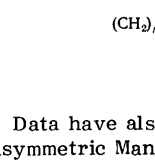
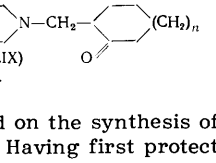
$n = 0, 1$

Having then removed the protecting group, the product was reintroduced into the Mannich reaction and the expected bisbase (XLIX) was obtained:



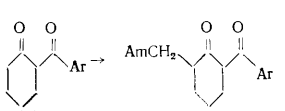
(XLIX)

Table 9. Aminomethylation of cyclohexanone and its derivatives.

Initial ketone	Reaction product	Yield, %	Biological activity	Refs.
 R=CH_3, C_6H_{11}, C_6H_9, C_6H_5, $C_6H_5CH_2$, $COOCH_3$, —	 Am=$N(CH_3)_2$, $N(C_2H_5)_2$, HNC_6H_5, NC_4H_8O, NC_5H_{10},	40—98	—	[56, 117, 147—149]
 R=H, CH_3, $CHCl_2$	 Am=NC_4H_8, NC_4H_8O, HC_5H_{10},	*	spasmolytic	[151]
 R^1=H, Cl, F, CH_3, CH O; R^2=H, Cl; R^3 H, CH_3O; R^4, R^5 H, CH_3	 Am=$HNCH_3$, HNC_2H_5, $N(CH_3)_2$, HNC_6H_{11}, $N(C_2H_5)_2$, NC_4H_8, NC_5H_{10}, NC_6H_{12}, $NHCH_2CH=CH_2$,	5—81	analgesic, tranquilising	[42]
 R=F, Cl, CH_3, CH_3O	 Am=$HNNH_2CH(CH_3)C_6H_5$, $HNCH(CH_3)CH_2C_6H_5$	30—67	action on central nervous system	[165]

*The yields are given in grams.

2-Aroylcyclohexan-1-ones (L) react under the conditions of the Mannich reaction with certain amines to form 6-aminomethyl-2-aroylcyclohexan-1-ones:[150]



(L)

Ar = C_6H_5, $C_6H_4OCH_3$-p, $C_6H_2(OCH_3)_3$-3, 4, 5; Am = NC_5H_{10}, $N(CH_3)_2$.

The aminomethylation of 3-aminocyclohex-2-en-1-one (LI) by piperidine hydrochloride and formaldehyde proceeds in accordance with the scheme[153]

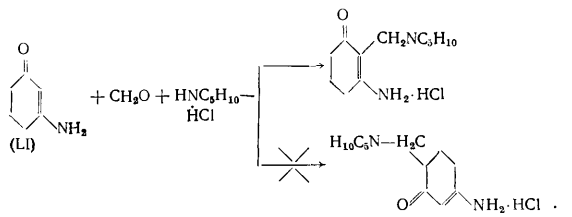
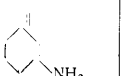
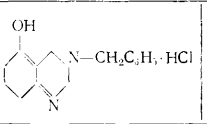
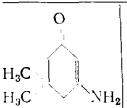
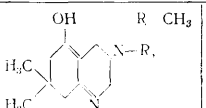
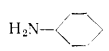
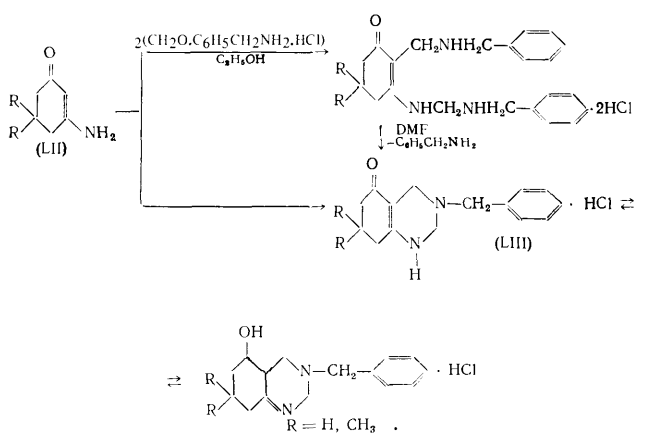


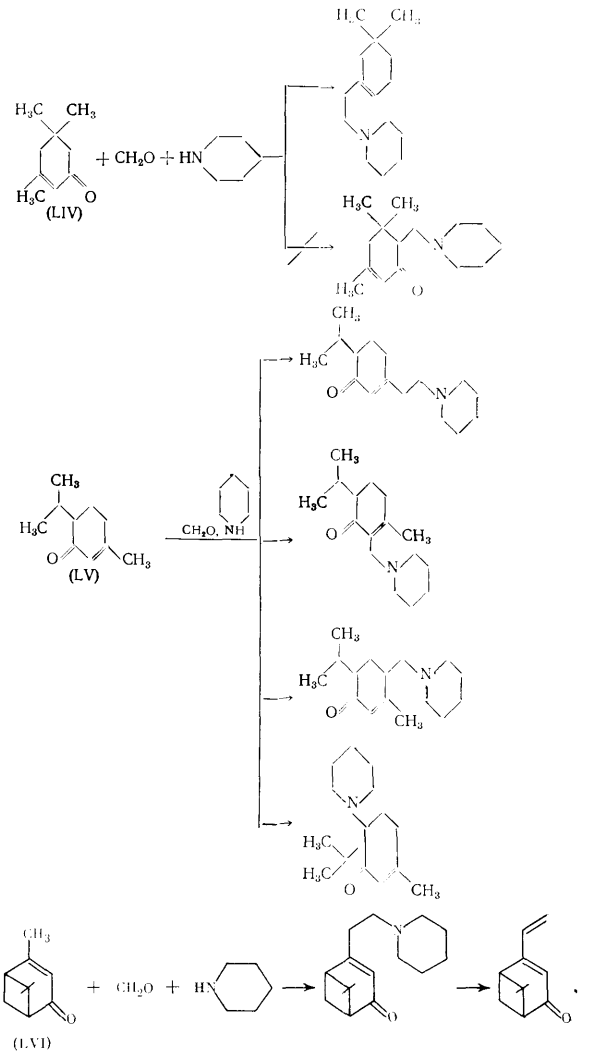
Table 10. Aminomethylation of substituted cyclohex-2-en-1-ones.

Enamine	Amine hydrochloride	Quinazoline derivatives	Yield, %
	$H_2NCH_2C_6H_5$		55,0
	H_2N-CH_3		42,0
		ditto, R = 	46,0
	$H_2N-CH_2-C_6H_5$	» , $R = CH_2C_6H_5$	64,0

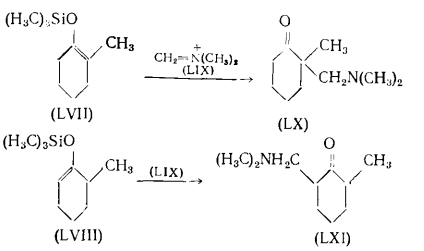
It has been shown that the product of the reaction of substituted cyclohex-2-enones (LII) with benzylamine hydrochloride (and other primary amines) and formaldehyde is a quinazoline derivative (LIII) (Table 10):[153]



The formation of vinylogues on aminomethylation of isophorone (LIV), piperitone (LV), and 2-pinen-4-one (LVI):

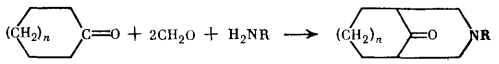


The regioselectivity of the reactions of the trimethylsilyl ethers of the enolic forms of cyclohexenone (LVII) and (LVIII) with the carbonium-immonium ion $[CH_2=\overset{+}{N}(CH_3)_2]$ (LIX) to form the Mannich bases (LX) and (LXI) in 65 and 78% yields respectively has been investigated and the authors established that compound (LXI) consists of a 2 : 1 mixture of stereoisomers[157].



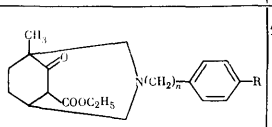
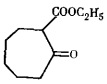
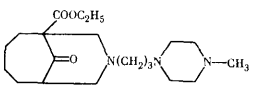
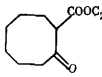
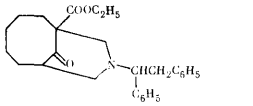
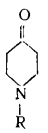
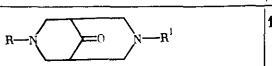
The condensation of substituted cyclic ketones with two moles of paraformaldehyde and one mole of a primary amine in acetic acid[158–160,162] or methanol[161] leads to the bicyclic

compound (LXII) (Table 11).

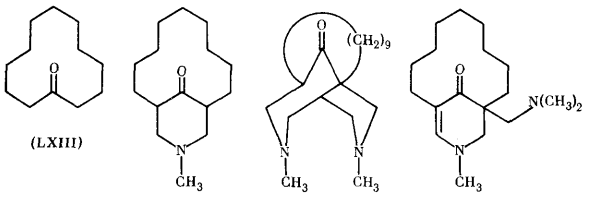


(LXII)

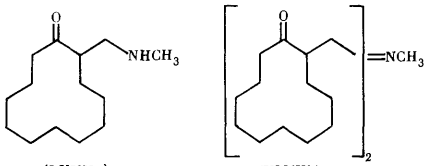
Table 11. The formation of bispidines on aminomethylation.

Initial ketone	Aminomethylation product	Yield, %	Biological activity	Refs.
	 $n = 1, 2$; R = H, F	10—27	analgesic, anti-inflammatory, hypotensive	[162]
		20	ditto	[162]
		8	»	[162]
 R=CH_3, $CH_2C_6H_5$, $(CH_2)_2C_6H_5$, *uзо*-C_3H_7	 R^1=$CH_2C_6H_5$, $(CH_2)_2C_6H_5$, C_6H_{13}, $(CH_2)_2OH$, alkyl(C_1-C_4), cyclopentyl, $(CH_2)_3N(CH_3)_2$, cyclohexyl	15—61	antiarrhythmic	[159-161]

Interesting data have been published on the aminomethylation of the cyclododecanone (LXIII).[163] Refluxing with formaldehyde and methylamine for two days resulting in the formation of a mixture of substances whose separation led to the isolation of the azabicyclopentadecanone (LXIV), the bispyridinediazatricyclopentadecanone (LXV), and the dihydropyridin-4-one (LXVI). On heating for less than two days, the products are the aminoketones (LXVIIa) and (LXVIIb):



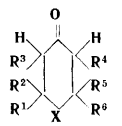
(LXIII) (LXIV) (LXV) (LXVI)

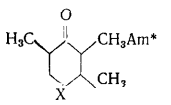
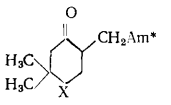
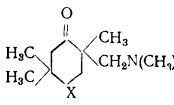
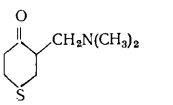
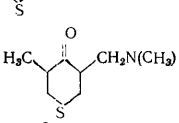
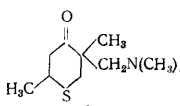
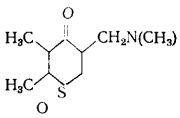


(LXVIIa) (XLVIIb)

Golovin and co-workers carried out a major study of the aminomethylation of saturated cyclic γ-ketones by formaldehyde and various amines as a function of the number and positions of the alkyl substituents relative to the carbonyl group and also the character of the heteroatom X in the ring (X = O, S, or N) [167-169,172-178] (Table 12).

Table 12. Aminomethylation of γ-ketones.

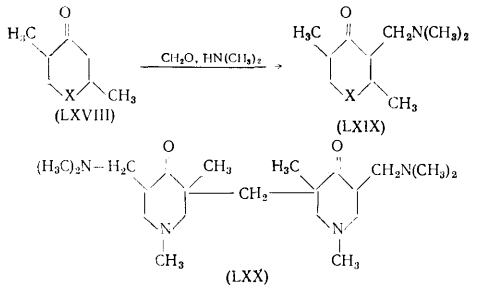


R^1	R^2	R^3	R^4	R^5	R^6	X	Aminomethylation product	Yield, %	Refs.
H	H	CH_3	H	H	CH_3	S, NCH_3		37—75	[167,168]
CH_3	CH_3	H	H	H	H	S,O, NCH_3		51—68	[169,172]
H	H	CH_3	H	CH_3	CH_3	O,S		56—61	[173]
H	H	H	H	H	H	S		56,5	[174]
H	H	CH_3	H	H	H	S		57	[175]
H	CH_3	H	CH_3	H	H	S		64	[178]
H	H	H	CH_3	H	CH_3	S		10—21	[177]

*Am = $N(CH_3)_2$, $N(C_2H_5)_2$, $N(C_3H_7)_2$, $N(C_4H_9)_2$, NC_4H_8, NC_4H_8O, NC_5H_{10}, NC_6H_{12}.

In the aminomethylation of 1,2,5-trimethylpiperidin-4-one (LXVIII, X = NCH_3), bis(1,2,5-trimethyl-3-dimethylaminomethyl-4-oxopiperidinyl)methane (LXX) was isolated together

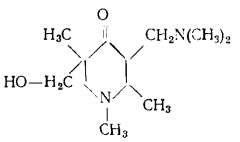
with the main reaction product (LXIX):[167-169]



(LXVIII) (LXIX) (LXX)

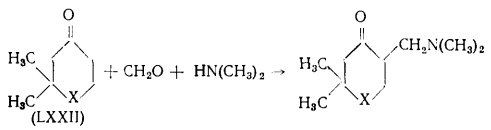
X = O, S ,

When the above reaction is carried out with a twofold excess of paraformaldehyde, 3-dimethylaminomethyl-5-hydroxymethyl-1,2,5-trimethyl-4-piperidinone (LXXI) is mainly formed:



(LXXI) .

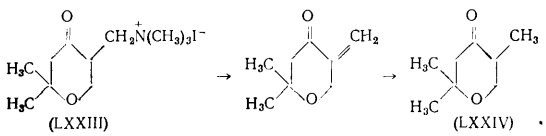
In order to elucidate the influence of two methyl groups in the β-position relative to the carbonyl group on the regioselectivity of the Mannich reaction, it was shown later[169] that, regardless of the nature of the entering aminomethyl group, the aminomethylation of compound (LXXII) proceeds with participation of only the methylene group located on the opposite side of the heterocycle relative to the methyl substituents:



(LXXII)

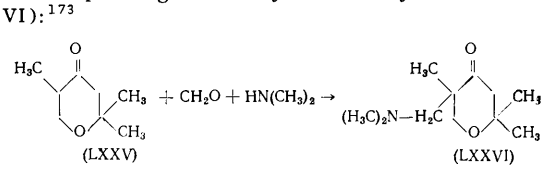
X = O, S, NCH_3 ,

Additional proof of the structure of the Mannich bases has been obtained[170] by exhaustive Hofmann methylation. For example, the methiodide of the aminoketone (LXXIII) has been converted by reductive deamination into the known 2,2,5-trimethyl-4-oxotetrahydropyran (LXXIV):[171]



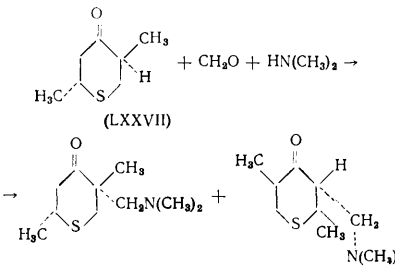
(LXXIII) (LXXIV) .

The study of the structural specificity of the aminomethylation of 2,2,5-trimethyl-4-oxotetrahydropyran (LXXV) showed that the reaction is directed exclusively to the tertiary carbon atom adjoining the carbonyl group and leads to the formation of the corresponding 5-dimethylaminomethyl derivatives (LXXVI):[173]



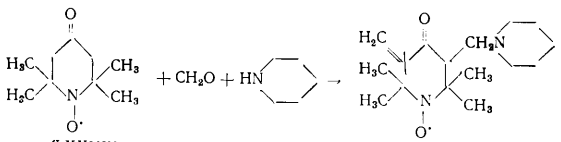
(LXXV) (LXXVI) .

The study of the products of the aminomethylation of *trans*-2e, 5e-dimethyl- and *cis*-3e, 5e-dimethyl-tetrahydro-1-thiopyran-4-ones (LXXVII) showed that only monoaminoketones with an axial orientation of the aminomethyl group are formed. The absence of bisaminomethyl bases from the reaction products in this instance can be explained by the impossibility of the entry of a second axial aminomethyl group next to the carbonyl group as a consequence of the *meta*-axial interaction[176]. It has been shown that the orientation of the aminomethylation depends exclusively on the structure of the initial ketone, namely on the number and positions of the alkyl substituents in the ring:



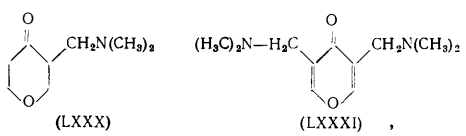
(LXXVII) .

It is of interest that the aminomethylation of 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxide (LXXVIII) results in the formation of compound (LXXIX) in 94% yield[179,180]:



(LXXVIII) (LXXIX) ,

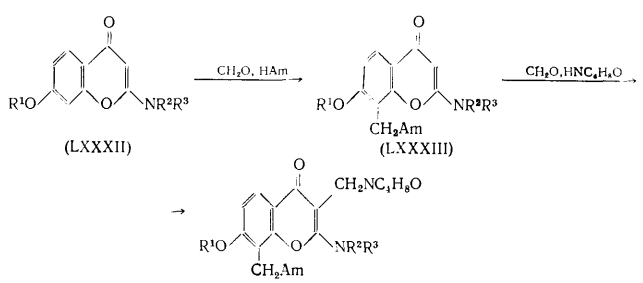
As early as 1952, Wiley[181] described the condensation of 4-pyrone with dimethylamine hydrochloride and formaldehyde in ethanol; the reaction product was identified as the monoaminoketone (LXXX). It was shown subsequently that both mono- and bis-dimethylaminomethylpyrones (LXXX) and (LXXXI) are formed[182]:



(LXXX) (LXXXI) ,

Table 13 lists the products of the aminomethylation of isoxazoles[183,184], pyrazoles[185], uracils[186], coumaranones[187], and other heterocyclic ketones[188-192]. A number of studies have been made on the aminomethylation of chromans, isochromans, and pyrans[193-204].

It has been shown[195] that the aminomethylation of chromans takes place in the 3-position. However, according to other data[196], in the case of 2-dialkyl-amino-7-hydroxychroman (LXXXII, R = H) substitution takes place in the 8-position with formation of compound (LXXXIII) and only the subsequent aminomethylation is in the 3-position with formation of compound (LXXXIV):

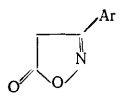
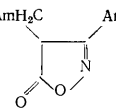
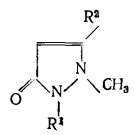
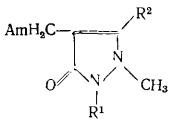
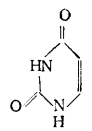
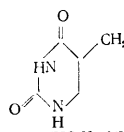
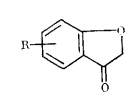
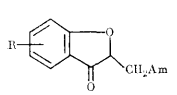
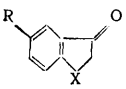
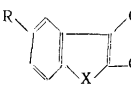
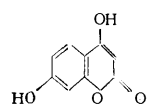
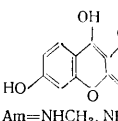
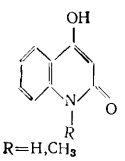
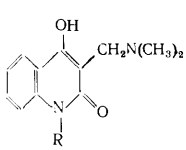
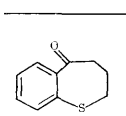
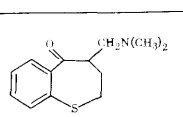
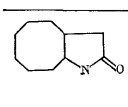
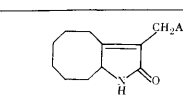


(LXXXII) (LXXXIII) (LXXXIV)

R^1 = H; Am = NC_4H_8O, NC_5H_{10},  NR^2R^3 = $N(CH_3)_2$, $N(C_2H_5)_2$, NC_5H_{10}, $N(CH_3)C_2H_5$, $N(C_2H_5)C_6H_5$;

R^1 = CH_3, Am = NC_4H_8O; NR^2R^3 = $N(C_2H_5)_2$, NC_4H_8, NC_5H_{10} .

Table 13. The Mannich reaction involving heterocyclic ketones.

Initial ketone	Aminomethylation product	Yield, %	Refs.
 Ar=C_6H_5, p-$NO_2C_6H_5$, p-ClC_6H_4, p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$	 Am=$N(CH_3)_2$, $N(C_2H_5)_2$, NC_4H_8, NC_4H_8O, NC_5H_{10}	70—96	[183, 184]
 R^1=CH_3, C_6H_5; R^2=H, CH_3	 Am=NC_4H_8O, $N(CH_2CH_2Cl)_2$	66—100	[185]
	 Am=NHC_4H_9, NHC_6H_{11}, $N(CH_3)_2$, NHC_6H_5, NHC_6H_4R(R=p-Cl, m-CH_3, p-CH_3O, p-NO_2)	30—98	[186]
 R=5-Cl, CH_3, NO_2, 7-Cl, CH_3	 Am=$N(CH_3)_2$, NC_4H_8O, NC_5H_{10}, $N(C_2H_5)_2$	22—78	[187]
 X=O, S, Se; R=H,CH_3	 Am=$N(CH_3)_2$, NC_4H_8, NC_5H_{10}	**	[188]
	 Am=$NHCH_3$, NHC_2H_5, NHC_3H_7, $NHCH_2CH{=}CH_2$, NC_5H_{10}	**	[189]
 R=H,CH_3		80	[190]
		23	[191]
	 Am=$N(CH_3)_2$, NC_4H_8O	**	[192]

*Using $>N^+ = CH_2Cl^-$ in acetonitrile at 20 °C.
**The yields are given in grams.

The side product (LXXXV) was also isolated:

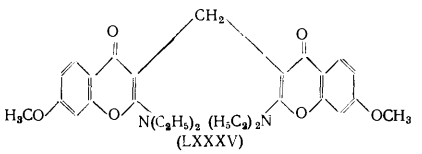
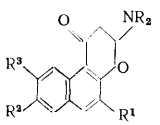
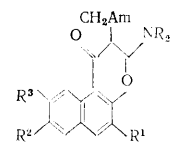
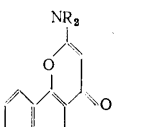
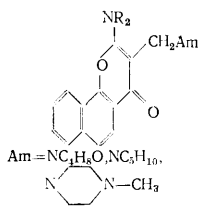
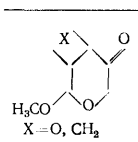
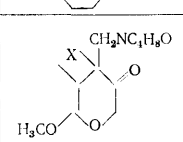
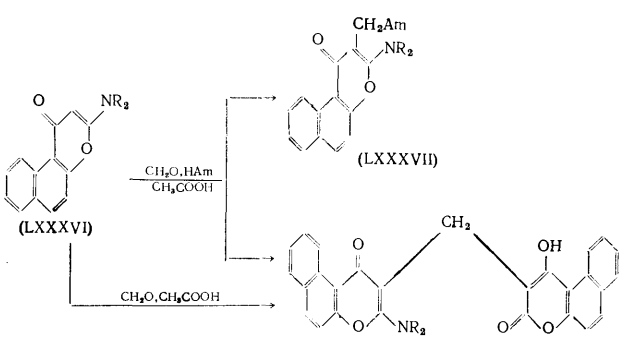

(LXXXV)

Table 14. Aminomethylation of 3-amino-1-oxo-1*H*-naphtho-[2,1-*b*]pyrans.

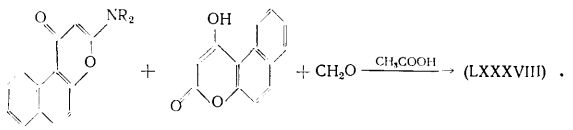
Initial ketone	Aminomethylation product	Yield, %	Biological activity	Refs.
 R^1=H, CH_3O; R^2=H,CH_3,Br, OAc;R^3=H,CH_3,OH,CH_3O, OAc;NR_2=$N(CH_3)_2$, $N(C_2H_5)_2$,$N(CH_3)C_2H_5$, NC_4H_8,NC_5H_{10}	 Am=NC_4H_8O,NC_5H_{10}	28—62	anti-convulsant	[201]
 NR_2=$N(CH_3)_2$, $N(C_2H_5)_2$, $N(CH_2)C_2H_5$	 Am=NC_4H_8O,NC_5H_{10},	21—54	neuro-tropic	[202]
 X=O, CH_2		70;88	—	[204]

The aminomethylation of 3-dialkylamino-1-oxo-1*H*-napntho-[2,1-*b*]pyrans (LXXXVI) in acetic acid leads to 2-dialkyl-aminomethylamino-1-oxo-1*H*-naphtho[2,1-*b*]pyrans (LXXXVII), which exhibit an anticonvulsant activity[198,199] (Table 14).

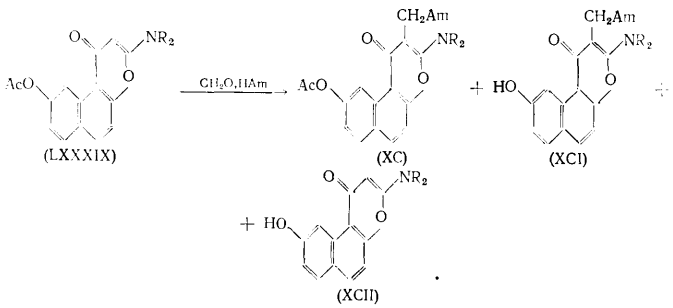

(LXXXVI) (LXXXVII) (LXXXVIII)

NR_2 = $N(CH_3)_2$, $N(C_2H_5)_2$, N (iso-C_3H_7)$_2$, NC_4H_8, NC_5H_{10}, $N(CH_2CH{=}CH_2)_2$, $N(CH_3)CH_2C_6H_5$, $N(C_2H_5)CH_2C_6H_5$;
Am = NC_4H_8O, NC_5H_{10} .

In the presence of an excess of acetic acid, 3-dialkylamino-2-{1-hydroxy-3-oxo-3*H*-naphtho[2,1-*b*]pyran-2-ylmethyl}-1-oxo-1*H*-naphtho[2,1-*b*]pyran (LXXXVIII) is formed as a side product. Its structure has been demonstrated by specific synthesis:



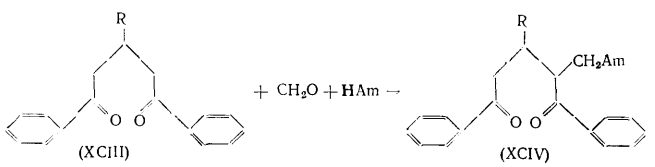
The aminomethylation of compound (LXXXIX) yielded a mixture of the three compounds (XC), (XCI), and (XCII):



6. Diketones

Comparatively few studies have been devoted to the aminomethylation of diketones[205–221] (Table 15).

Thus Tilichenko and co-workers showed that the aminomethylation of the diketones (XCIII) yields only the monoaminomethyl derivatives (XCIV):[205–212]



The condensation of 1-(2-oxocyclohexyl)-1,3-diphenyl-3-propanone (XCV) with formaldehyde and dimethylamine hydrochloride results in the formation of a mixture of 2-dimethylaminomethyl-1-(2-oxocyclohexyl)-1,3-diphenyl-3-propanone (XCVI) and 1-(3-dimethylaminomethyl-2-oxocyclohexyl)-1,3-diphenyl-3-propanone (XCVII):[209]

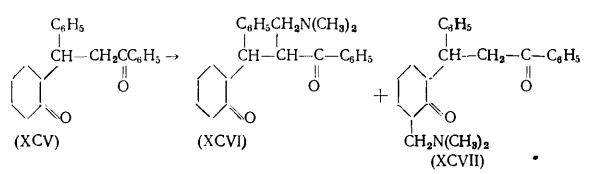
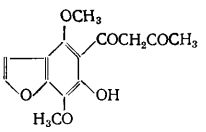
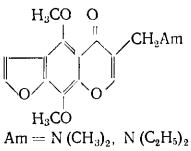
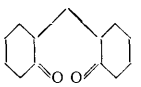
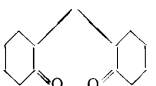
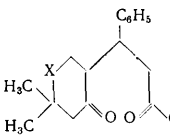
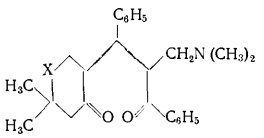
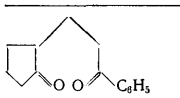
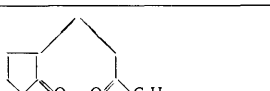
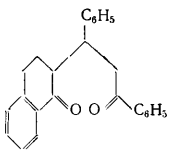
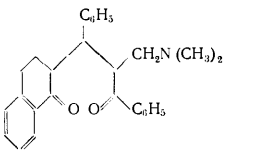
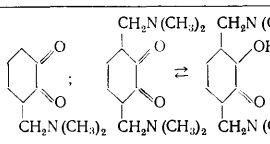
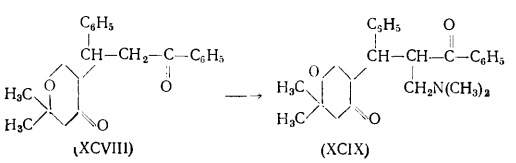


Table 15. The Mannich reaction involving diketones.

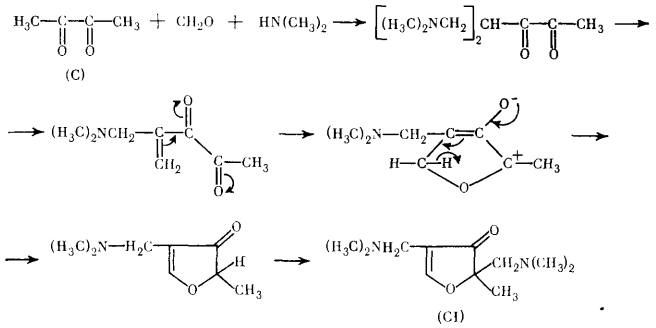
Initial ketone	Aminomethylation product	Yield, %	Refs.
	 Am = N $(CH_3)_2$, N $(C_2H_5)_2$, NC_5H_{10}		[219]
	 Am = N $(CH_3)_2$, N $(C_2H_5)_2$	48—100	[212]
 X = O, S, CH_2		70—83	[210, 211]
	 Am = N $(CH_3)_2$, NC_4H_8O	50; 70	[211]
		59	[211]
		24	[213]

On the other hand, the aminomethylation of 1-(α,α-dimethyltetrahydro-γ-pyron-β′-yl)-1,3-diphenyl-3-propanone (XCVIII) in the ring is not observed; only 2-dimethylaminomethyl-1-(α,α-dimethyltetrahydro-γ-pyron-β′-yl)-1,3-diphenyl-3-propanone (XCIV) is produced[210,212]:

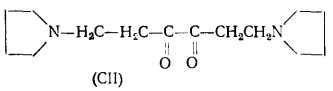


When the Mannich reaction is carried out with butane-2,3-dione (C), the character of the product obtained depends on the nature of the amino-component[213]. Thus the product

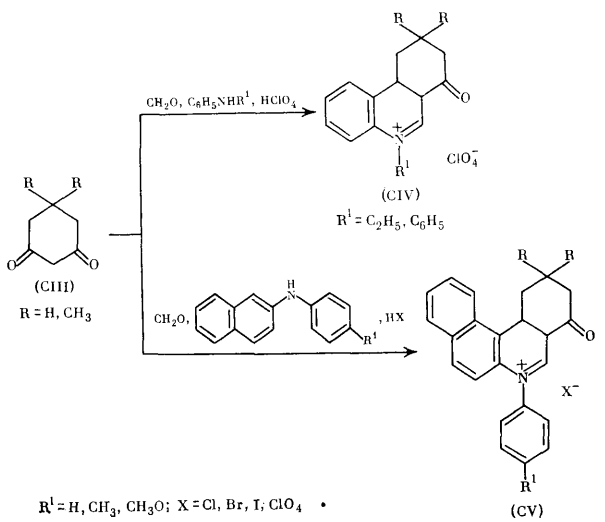
of the condensation of butane-2,3-dione with paraformaldehyde and dimethylamine is 2-methyl-2,4-bis(dimethylaminomethyl)-3-furanone (CI) in 18% yield, whose formation can be represented as follows:



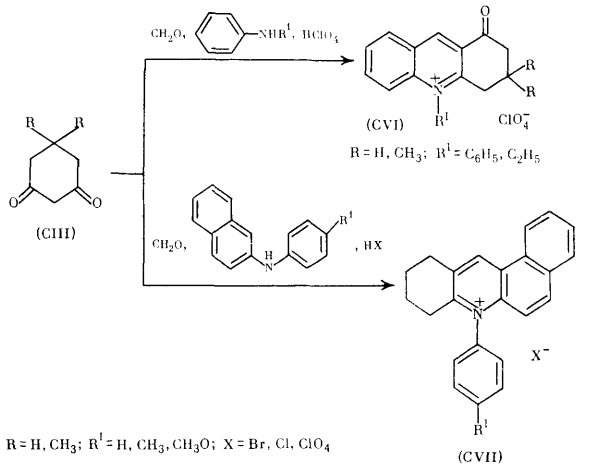
When compound (C) reacts with pyrrolidine, the diaminoketone (CII) is formed in 44% yield:



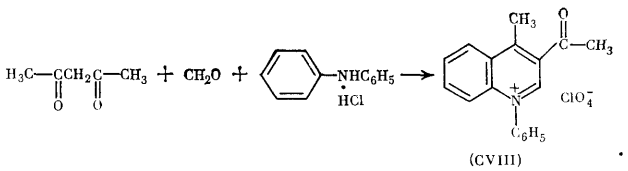
Secondary aromatic amines of the benzene series cyclise with paraformaldehyde and dimedone (CIII, R = CH_3) in the presence of perchloric acid to form the *N*-substituted quaternary 9,9-dimethyl-7-oxo-7,8,9,10-tetrahydrophenanthridinium salts (CIV). Phenyl(*p*-X-phenyl)-2-naphthylamines cyclise in the presence of hydrochloric, hydrobromic, and perchloric acids to form *N*-aryl-substituted 2,2-dimethyl-4-oxo-1,2,3,4-tetrahydrobenzo[*a*]phenanthridinium salts (CV):



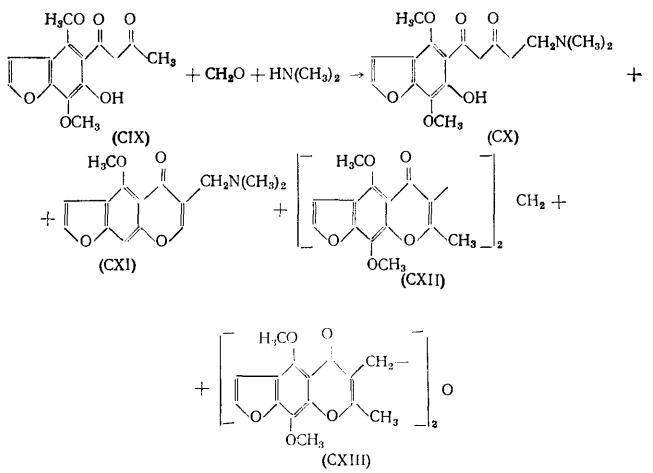
The condensation of diphenylamine and *N*-ethylaniline with formaldehyde and cyclic β-diketones (CIII) leads to the formation of *N*-substituted 1-oxo-1,2,3,4-tetrahydroacridinium salts (CVI). The authors' more detailed studies of the products of the reaction with 2-arylaminonaphthalenes showed that the cyclisation involves the most reactive α-position of the naphthalene ring, which leads to the formation of quaternary 11-oxo-8,9,10,11-tetrahydrobenzo[*a*]acridinium salts (CVII):[215]



Acetylacetone reacts with formaldehyde and diphenylamine in the presence of perchloric acid to form 3-acetyl-1-phenyllepidinium perchlorate (CVIII):[216]



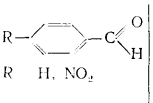
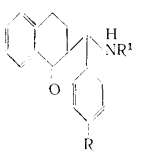
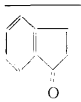
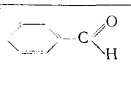
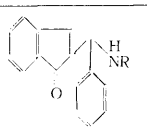
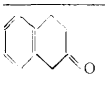
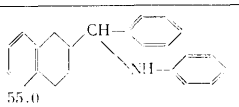
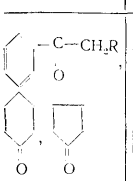
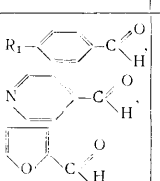
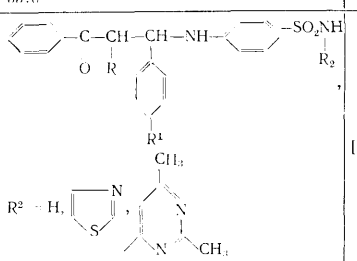
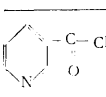
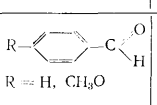
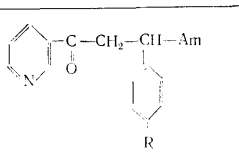
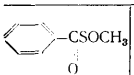
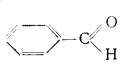
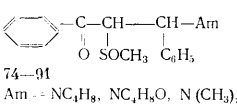
The aminomethylation of ω-acetylkhellinone (CIX) leads to the formation of the cyclisation product (CXI) and the dimerisation products (CXII) and (CXIII) in addition to the main product (CX):[217–219]



III. THE MANNICH REACTIONS WITH ALDEHYDES

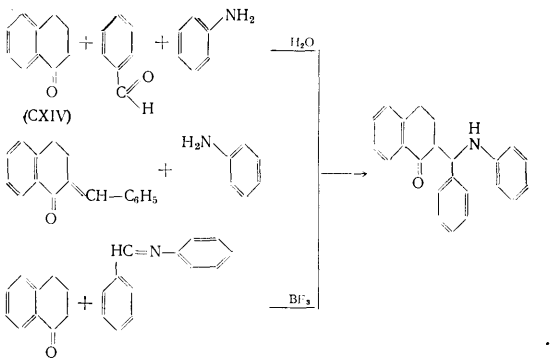
A number of studies have been devoted to the aminomethylation of ketones by various aldehydes[111,166,222–226] (Table 16).

Table 16. The Mannich reaction involving various aldehydes.

Initial ketone	Initial aldehyde	Aminomethylation product [yield, %]	Refs.
	 R = H, NO_2	 52–100* R^1 = C_6H_5, $C_6H_5OCH_2$-*p*	[222]
		 93, 97* R = C_6H_5, $C_6H_4OCH_3$-*n*	[222]
	ditto	 55.0	[166]
 R = H, CH_3	 R^1 = H, CH_3O, NO_2	 R^2 = H, 31–94	[111]
	 R = H, CH_3O	 20–100 Am = NHC_3H_5, NHC_5H_{11}, NC_5H_{10}, NC_4H_8O, $NHCH_2C_6H_5$, $NH(CH_2)_2C_6H_5$	[223]
		 74–91 Am = NC_4H_8, NC_4H_8O, $N(CH_3)_2$	[224]

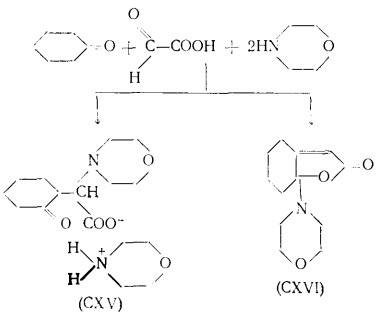
*The reaction was carried out in the presence of a catalyst (BF_3).

In particular, when the α-tetralone (CXIV) is condensed with benzaldehyde and amines, substitution takes place in the 2-position, which has been demonstrated by specific synthesis[218]:



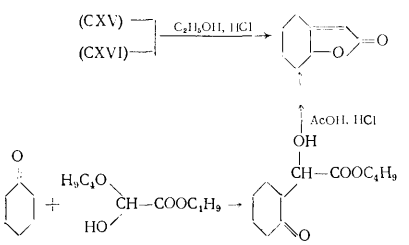
(CXIV)

On the other hand, the condensation of cyclohexanone, morpholine, and glyoxalic aldehyde results in the formation of a mixture of products (CXV) and (CXVI):[214]

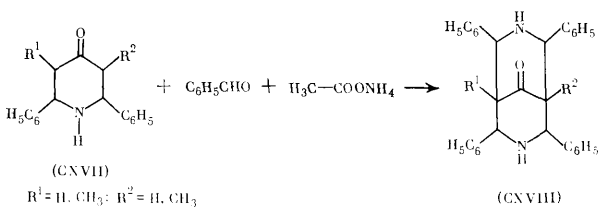


(CXV) (CXVI)

The formation of compounds (CXV) and (CXVI) has been demonstrated as follows:



When benzaldehyde is used in the Mannich reaction instead of formaldehyde, the substituted piperidinones (CXVII) are converted into aza- and diaza-bicyclo[3.3.1]nonan-9-ones (CXVIII):[226]

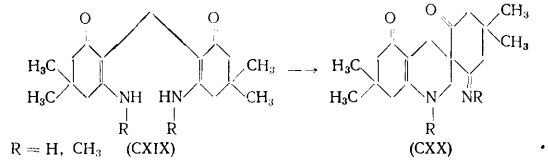


(CXVII) R^1 = H, CH_3; R^2 = H, CH_3 (CXVIII)

It has been shown[226] that compound (CXVII, $R^1 = R^2 = CH_3$) does not form a bicyclic product despite the presence of two axial α-hydrogen atoms. Steric hindrance generated by the tertiary carbon atoms C(3) and C(5) operates in this instance.

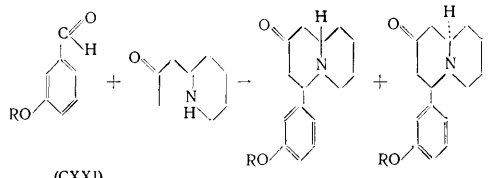
Not three but only two components, one of which plays the role of both the amino- and the CH-acid component, can enter into the Mannich reaction. Similar condensations,

i.e. intramolecular Mannich reactions, have been investigated in other studies[227–229]. In particular, it has been shown that methylenebisenaminoketones (CXIX) condense with formaldehyde to form the spiro-compounds (CXX):[227]



R = H, CH_3 (CXIX) (CXX)

The condensation of isopelletierine (CXXXI) with 3-methoxybenzaldehyde in an aqueous medium leads to the formation of *trans*- and *cis*-quinolizidines (CXXII) and (CXXIII) in proportions of 1:6, while the reaction with 3-hydroxybenzaldehyde leads almost exclusively to *trans*-quinolizidine (CXXIV).[229] On the other hand, in methanol the reaction proceeds with formation of compounds (CXXII) and (CXXIII) in proportions of 5:1. It has been shown that the interaction of compound (CXXI) with an arylaldehyde in an alkaline medium leads to the formation of *cis*-4-aryl-quinolizidin-2-one, which then isomerises to the corresponding *trans*-form:



(CXXI) (CXXII), R = CH_3 (CXXIII)
R = H, CH_3 (CXXIV), R = H

The data presented in this review on the synthesis of β-aminoketones show that more detailed studies of the Mannich reaction would be useful. This is due to the extensive possibilities for its application in organic synthesis and in particular in the specific synthesis of compounds with a potential biological activity.

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Mndzhoyan Institute of Fine Organic Chemistry,
Academy of Sciences of the Armenian SSR, Erevan

Translated from *Uspekhi Khimii*, 53, 1014-1044 (1984) U.D.C. 542.91 + 547.834.2

Total Synthesis of 8-Azasteroids

F.A.Lakhvich, L.G.Lis, and A.A.Akhrem

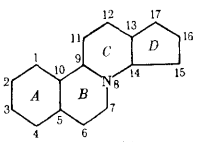
Studies on the total synthesis of 8-azasteroids from the start of investigations in this field (1963) up to 1983 are examined. Earlier studies on the synthesis of compounds formally containing the 8-azasteroid skeleton and those on the synthesis of 8-azasteroids with an additional heteroatom are also analysed. Data are presented on the stereochemistry and biological activity of these compounds.
The bibliography includes 148 references.

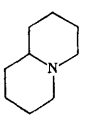
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I. INTRODUCTION

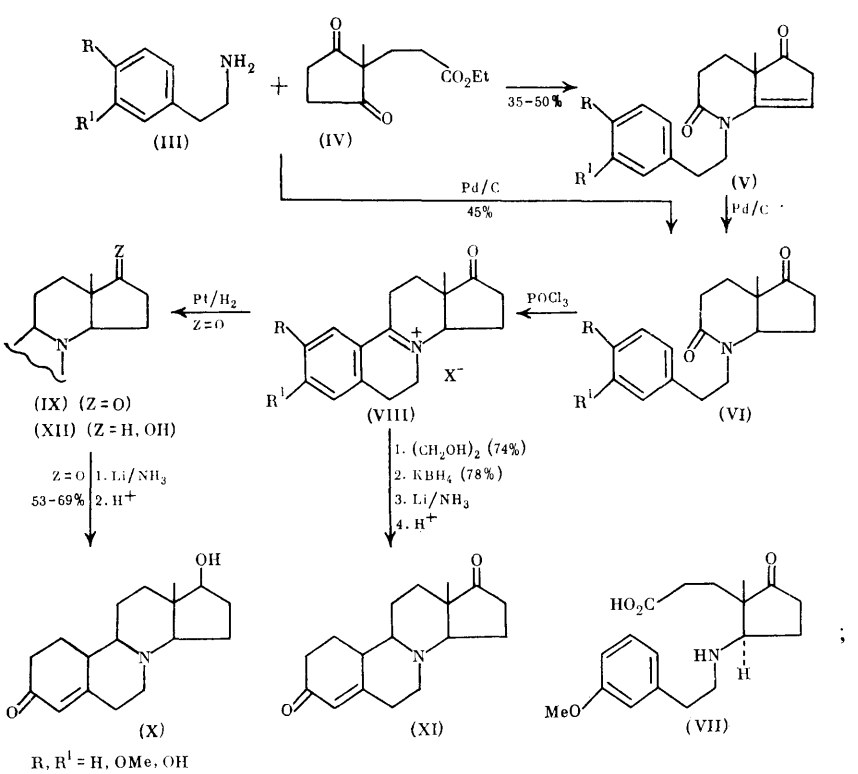
8-Azasteroids include compounds with a partly or fully hydrogenated cyclopentanophenanthrene skeleton (I) in which the carbon atom in the 8-position has been replaced by nitrogen:


(I)


(II)

Compounds of this type have not been found in nature and all the known derivatives of this class are synthetic products. The development of studies on the synthesis of 8-azasteroids is due to a number of factors. It was postulated that the introduction of a heteroatom, entailing significant changes in the geometry of the molecule, would make it possible to obtain new hormonal preparations. However, in general this hypothesis was not confirmed and the compounds obtained possessed only a weak hormonal activity or lacked it altogether and the main efforts of investigators were then directed to the search, among compounds of this series, for those possessing a biological activity resembling that of steroids in

Scheme 1



the absence of hormonal activity. This would make it possible to replace in clinical practice many steroid preparations whose application is complicated by their hormonal activity. Significant advances have been made on these lines. This stage of the development of the chemistry of heterosteroids is therefore characterised by the abandonment of the synthesis of structurally closest heteroanalogues of natural steroids and an increase of the number of studies on the synthesis of 8-azasteroids with an additional heteroatom, additional rings, and other derivatives with substituents and stereochemistry unusual for natural steroids.

On the other hand, 8-azasteroids can be regarded as derivatives of the heterocyclic compound quinolizidine (II), whose fragment is incorporated in the main structural unit in many structural compounds. The structural similarity of formula (I) to heterocycles of the quinolizidine series makes it possible to employ earlier data on both the synthesis and stereochemistry of the latter in studies on 8-azasteroids. On the other hand, certain investigations of the synthesis of heterocyclic systems, formally leading to the formation of the 8-azasteroid skeleton, did not deal with the latter as such and have therefore escaped the notice of investigators. Only isolated studies on 8-azasteroids have been briefly considered in the existing reviews on heterocyclic steroids[1-4].

This review is the first attempt at a survey of studies devoted to the direct synthesis, stereochemistry, and biological activity of 8-azasteroid compounds. It presents data both on the synthesis of close 8-aza-analogues of natural steroids (Section II) and on the formal construction of the 8-azasteroid skeleton, including derivatives with two and more aromatic rings (Section III) or with an additional heteroatom (Section IV).

II. COMPOUNDS WITH ONE HETEROATOM

The first studies on the total synthesis of 8-azasteroids were published in 1963. Meltzer's group was able to obtain *dl*-8-azaoestrone and its stereoisomers[5] (Scheme 1). A key failure of this scheme is the condensation of β-phenylethylamines (III) with a diketone (IV), which leads to the unsaturated lactam (V). Catalytic hydrogenation of the latter takes place sterospecifically, giving rise to a high yield of the lactam (VI) with a *cis*-C/D-junction. The same product has been obtained in a single stage by the reductive condensation of the amine (III) and the diketoester (IV). The aminoacid (VII) was obtained as a side product of the condensation and was converted at the melting point into the *trans*-C/D-lactam (VI). The Bischler–Napieralski cyclisation of both isomeric lactams made it possible to obtain the quaternary salts (VIII), which have been isolated as the corresponding *cis*- and *trans*-perchlorates. Catalytic hydrogenation of the *cis*-perchlorate leads to a mixture of the *syn*- and *anti*-H(9)/CH_3(13)-isomeric bases (IX) with a *cis*-C/D-junction. Under the same conditions, the *trans*-perchlorate gives rise to the *trans*-C/D-isomer (IX) with the *anti*-orientation of H(9) and CH_3(13).

Treatment of each isomer of the 3-methoxy-derivative (IX) with 48% HBr leads to the corresponding stereoisomers of 8-azaoestrone, which have been isolated in the form of the hydrobromides. Among the compounds obtained the *anti, trans, trans*-isomer† is *dl*-8-azaoestrone. The configurational assignments were based on the study of molecular models, infrared spectra, rates of oxidation, and subsequently the study of ^{1}H NMR spectra[6]. X-Ray diffraction data for the hydrobromide of *dl*-8-azaoestrone confirmed the validity of the assignments for each isomer[7]. Detailed studies of the stereochemistry of the compounds obtained by ^{1}H NMR[6] led the authors to an erroneous alteration of the assignments for the *cis*-C/D-isomers, but subsequently[8], after the synthesis of the fourth isomer, these assignments were corrected. In particular, it was found that the Bhacca–Williams correlations[9], which established the position of the angular substituent from the change of its chemical shift on passing from chloroform to benzene, are inapplicable to the 8-azasteroid series.

In the synthesis of the isomer with the *trans*-C/D-junction[6], the lactam (V) was reduced with potassium tetrahydroborate and subsequent catalytic hydrogenation to form the saturated 17β-alcohol which gives rise to the *trans*-C/D-lactam (VI) as a result of the Jones oxidation in 27% yield relative to the initial diketoester (IV).

The Birch reduction of the methyl ether of 8-azaoestrone (IX) (*trans*-C/D) followed by acid hydrolysis yielded compounds of the 8-aza-19-nortestosterone (X) series. 8-Aza-19-norandrostenedione (XI) was obtained analogously from the quaternary salt (VIII). In compounds (XI) and (X) the β-orientation was attributed to the hydrogen at C(10) on the basis of the known fact that acid treatment of the Birch reduction products results in the formation of more stable isomers having this configuration.

The reduction of each of the three stereoisomers of 8-azaoestrone with lithium tetrahydroaluminate proceeds stereospecifically to form the corresponding isomeric 8-azaoestradiols (XII). The α-orientation has been attributed to the 17-hydroxy-group in the compounds obtained from the *cis*-C/D-isomers and the β-orientation was attributed to the corresponding group in the compounds obtained from the *trans*-C/D-isomer, and the structure of the latter was confirmed by X-ray diffraction[10].

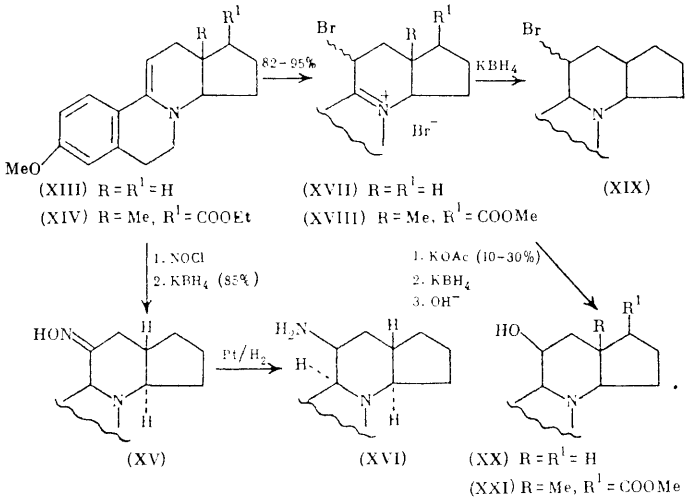
The scheme for the total synthesis of 8-azaoestrone examined above was also used to synthesise 17-deoxy-compounds[11].

In the course of further studies on the modification of 8-azasteroids, a method was developed for the introduction of the 11-hydroxy- and 11-amino-groups[12] (Scheme 2). When the tetracyclic enamine (XIII) is treated with nitrosyl chloride, the 11-nitroso-adduct is formed and its reduction leads to the oxime (XV). Catalytic hydrogenation of both the nitroso-derivative and of the oxime gives rise to the diamine (XVI) with a *trans*-quinolizidine junction and an axial amino-group. The attempts to hydrolyse compound (XV) under various conditions for the subsequent introduction of the 11-hydroxy-group were unsuccessful. A method was therefore developed involving the low-temperature bromination of the enamines (XIII) and (XIV) to give a mixture of the quaternary salts (XVII) and (XVIII) respectively, epimeric with respect to C(11). The reduction of the salt (XVII) with tetrahydroborate leads to the bromide (XIX), which, however, was resistant to nucleophilic substitution reactions. It was found that treatment of the quaternary salts (XVII) and (XVIII) with potassium acetate followed by reduction and hydrolysis leads to the aminoalcohols (XX) and (XXI), the former being obtained in the form of a mixture of three of the four possible isomers with respect to C(9) and C(11) (two *trans*-B/C and one cis-B/C), while the latter was obtained as the sole isomer with a *trans*-quinolizidine junction and an axial 11-hydroxy-group. Another pathway leading to analogous results but with a higher yield consists in the treatment of the quaternary salts (XVII) and (XVIII) with silver nitrate to form the corresponding 11-oxo-derivatives, whose subsequent reduction leads to a mixture of two isomeric bases (XX)

† Here and henceforth the terms *anti(syn)*-, *trans(cis)*-, and *trans(cis)*- refer to the orientation of H(9) and CH_3(13) [or H(13)] in the first case, to the B/C-junction in the second, and to the C/D-junction in the third.

in the former case and of a single base (XXI) in the latter. The stereochemistry of the compounds obtained was deduced from infrared and ^{1}H NMR spectroscopic data.

Scheme 2



(XIII) R = R^1 = H
(XIV) R = Me, R^1 = COOEt
(XVII) R = R^1 = H
(XVIII) R = Me, R^1 = COOMe
(XIX)
(XV)
(XVI)
(XX) R = R^1 = H
(XXI) R = Me, R^1 = COOMe

8-Aza-analogues of 19-norprogesterone have been synthesised by a method[13] analogous to that for the synthesis of 8-azaoestranes and 8-aza-androstanes[5,6], as shown in Scheme 3. The introduction of the pregnane side chain was achieved by the Arens–Van Dorp method or the Corey method. In the first procedure the aminoester (XXII) is subjected to acid hydrolysis followed by treatment with methyl-lithium. The Birch reduction of the resulting ketone in the form of the ethylene ketal yields two 8-aza-19-norprogesterones (XXIV) epimeric with respect to C(17).

In the second method, the ketosulphoxide (XXIII) is obtained by the reaction of the ester (XXII) and the anion of dimethyl sulphoxide and its subsequent cleavage gives rise to 8-aza-19-norprogesterone (XXIV) with a 17β-acetyl group.

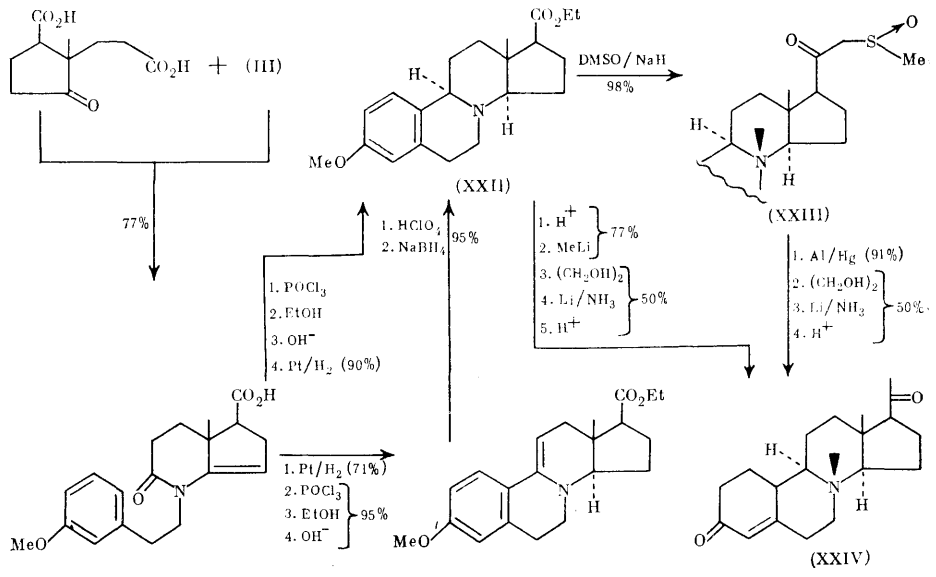
Two alternative methods have been used for the introduction of the 17-hydroxy-group, making it possible to obtain selectively either the 17α- or the 17β-hydroxy-derivative[13]. In the first procedure the ketolactam (XXVI) was converted into the aminoester (XXV), as shown in Scheme 4. Treatment of the latter with the anion of dimethyl sulphoxide yields a β-ketosulphoxide, whose cleavage with aluminium amalgam results in the formation of the ketoalcohol (XXVI). Protection of the 20-oxo-group with subsequent Birch reduction and acid hydrolysis gives rise to 17α-hydroxy-8-aza-19-norprogesterone (XXVII).

The synthesis of the 17β-hydroxy-compounds consists of the following steps. The reaction of the ketolactam (VI) with ethynylmagnesium bromide and subsequent hydration give rise to the ketone (XXVIII), from which 17β-hydroxy-8-aza-19-norprogesterone (XXIX) was obtained by the sequence of reactions presented in the Scheme.

In order to introduce the 21-hydroxy-group, a method was developed for the modification of the corticoid side chain using the Pummerer rearrangement[14]. Treatment of the esters (XXX) with the anion of dimethyl sulphoxide by Corey's method yields the 17β-ketosulphoxide (XXXI), whose rearrangement takes place on heating in acetic acid to form the acetate of the hemimercaptal (XXXII). Desulphurisation of the latter leads to the 21-acetoxy-derivative (XXXIII). Compound (XXXd), used in this Scheme, has been obtained from the quaternary salt of the ester (XXXIV) by the method described previously[12].

The method of synthesis of 17-deoxy-12-oxo-8-azasteroids by the *AB* + *D* → *ABCD* scheme was proposed by Meyers' group[15] (Scheme 5). Condensation of the aminoesters (XXXV) with the cycloalkanones (XXXVI) leads to the tetracyclic enaminoketones (XXXVII),[16] whose reduction gives rise to the aminoketone (XXXVIII). Treatment of the enaminoketone (XXXVII) with an excess of methyl iodide leads to a mixture of the *C*- and *O*-alkylated salts (XXXIX) and (XL) in proportions of 9 : 1. Catalytic hydrogenation of the quaternary salt (XXXIX) yields the methyl ether of 17-deoxy-12-oxo-8-azaoestrone (XLI) in the form of a mixture of two isomers, whose configuration was established by X-ray diffraction and infrared and ^{1}H NMR spectroscopy#.

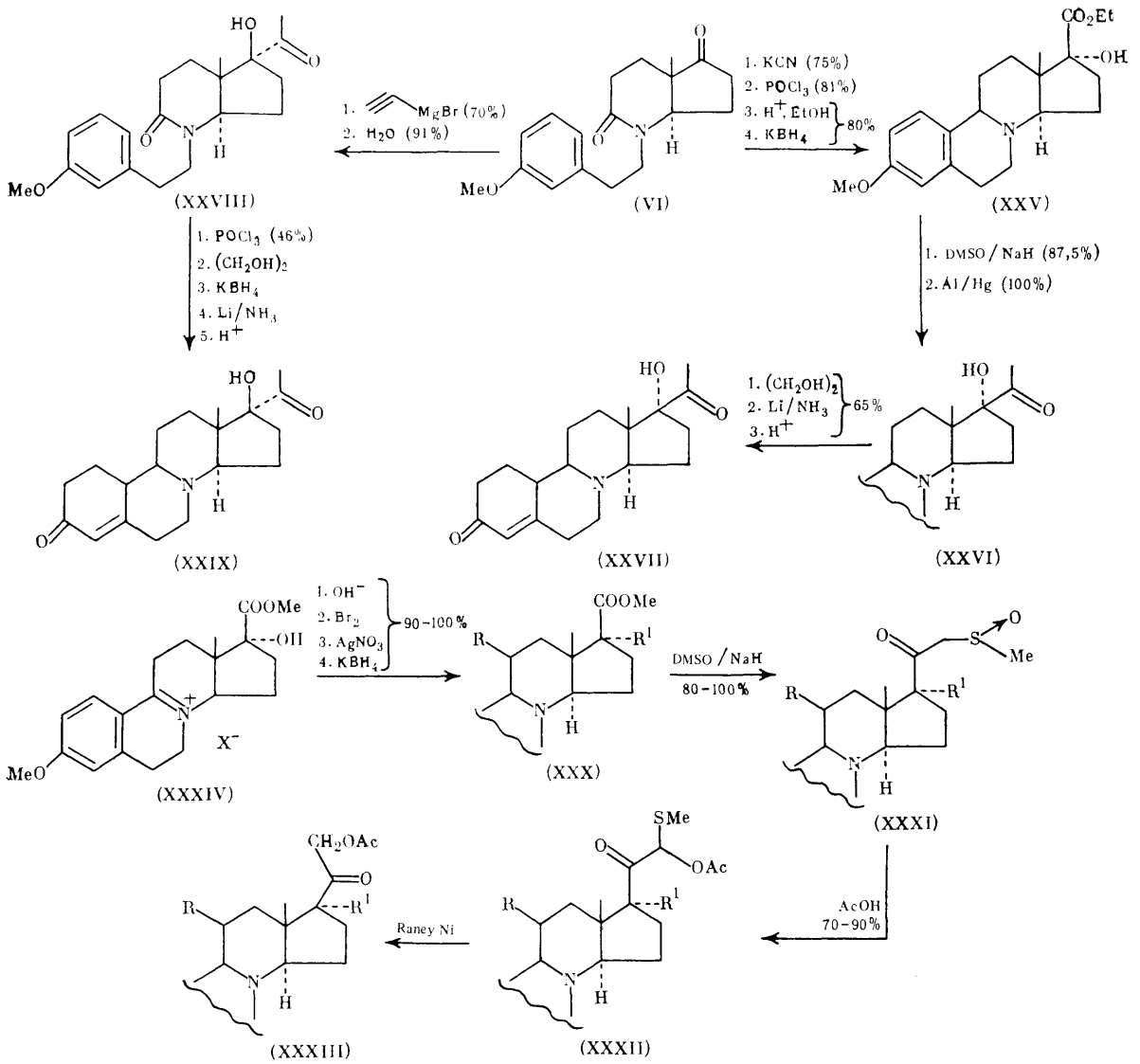
Scheme 3



(XXII)
(XXIII)
(XXIV)

Initially incorrect configurations were erroneously attributed to these compounds[17,18], but these were corrected after X-ray diffraction studies[8,19].

Scheme 4



(a) $R = R^1 = H$; (b) $R = H$, $R^1 = OH$; (c) $R = OH$, $R^1 = H$; (d) $R = R^1 = OH$.

The stereochemistries of the bases (XLI) and (IX) were compared by the specific reduction of these compounds to the deoxy-derivatives (XLII). The replacement of the β-aminoester (XXXV) by the β-aminonitrile also makes it possible to obtain the enaminoketone (XXXVII). Under these conditions, the yields were somewhat lower at all stages for $n = 1$ and 3 than for $n = 2$.[25]

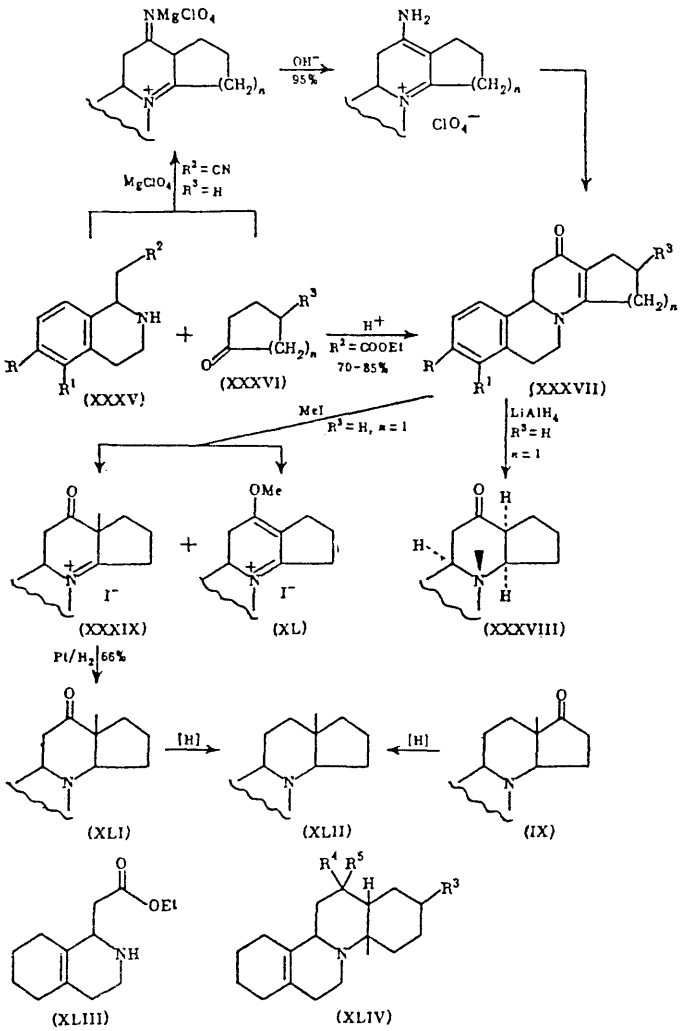
Using the octahydroisoquinoline ester (XLIII) as the *AB* fragment in the condensation with cycloalkanones, compounds of type (XXXVII) with a $\Delta^{5(10)}$-bond were obtained and their modification at C(12) and addition of a Grignard reagent to the $\Delta^{13(14)}$-bond give rise to the derivative (XLIV).[20] Analogous studies have been carried out using different ketones (XXXVI) with rings containing between 5 and 15 atoms[21].

The condensation of β-aminoesters of type (XXXV) with cycloalkanones was investigated on model compounds[22] and the dependence of the rate of reaction and of the yield of the product on the nature of the departing group (the ester residue) was established. The conditions for the angular alkylation of cisoid enaminoketones were investigated on tricyclic *BCD* model compounds[23,24].

The synthesis of the methyl ether of 8-azaoestrone and its analogues was developed by the same workers using the method presented in Scheme 6.[26] The unstable immonium salt (XLVI) is hydrogenated over the Adams catalyst to form a mixture of the methyl ether of 8-azaoestrone (IX) and its stereoisomer, to which the *syn,trans.cis*-configuration was subsequently assigned[8]§.

§ The *anti,trans,cis*-configuration was initially attributed to this compound[26].

Scheme 5



When $n = 2$ and R = H, the transoid enaminoketones (XLVII), obtained previously by Nelson and Tamura[27], is formed. The hydrogenation of its immonium salt (XLVI) gives rise to the aminoalcohol (XLVIII), whose Jones oxidation leads to the methyl ether of 18-nor-D-homo-8-azaoestrone (XLIX).

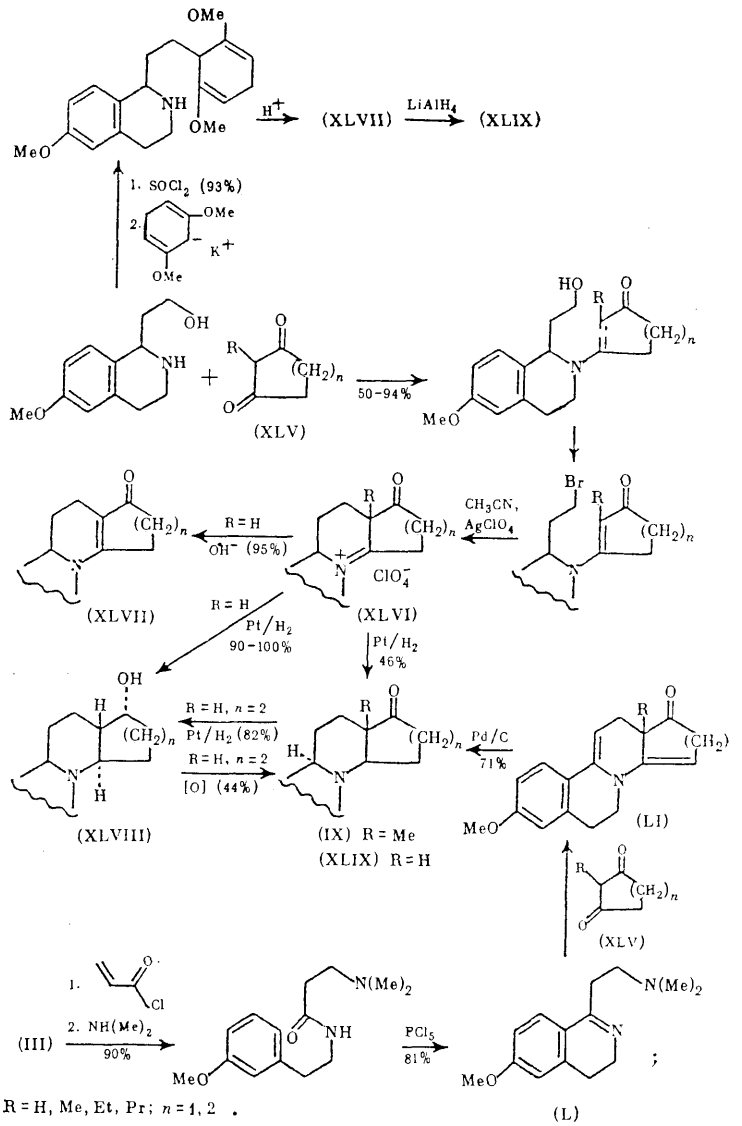
Clarkson's synthesis of 8-azaoestrone and its D-homo-analogue was based on the Michael reaction between the diamine (L) and the β-diketones (XLV) [28] (Scheme 6). The reaction proceeds with simultaneous cyclisation to form the enamines (LI), whose catalytic hydrogenation leads to the aminoketones (IX) and (XLIX). When the latter are fused with pyridine hydrochloride, 8-azaoestrone or its D-homo-analogue are formed. A *cis*-C/D-junction with β-orientation of the benzyl proton was attributed, on the basis of the results of the oxidation with mercury acetate, to the second isomeric ketone obtained on reduction of the enamine (LI) ($n = 2$).

The methyl ether of 8-aza-D-homo-18-noroestrone was synthesised by the method presented in Scheme 6.[27] The reduction of the enaminoketone (XLVII) with lithium tetrahydroaluminate leads to a mixture of two isomeric ketones (XLIX) with a *trans*-B/C-junction, which are epimers with respect to C(13), since one of the isomers is converted into the other on treatment with a base. However, the configurations of the isomers were not established.

Subsequently various details of 8-aza-19-nortestosterone, (X) and (LIII), were obtained[29] from the enamine (LI) and the methyl ether of 8-azaoestrone (IX) (Scheme 7). In order to investigate the biological activity, various substituents were introduced into the 17-position of the 8-aza-19-nortestosterone molecule. 17α-Substituted derivatives of 8-aza-19-nortestosterone (LIII) were then obtained from compound (IX). The above methods are inapplicable to the synthesis of 17α-ethynyl derivatives (LIII). They were synthesised by the Oppenauer oxidation of the aminoalcohol (LV) with subsequent ethynylation and hydrolysis.

8-Aza-19-norprogesterone (XXIV) and its analogues were obtained from the aminoketone (IX) via stages involving the formation of the ethylidene derivative (LVII) and the methylmethanol (LVIII).[30] The 13-ethyl derivatives were synthesised in accordance with the same scheme.

Scheme 6

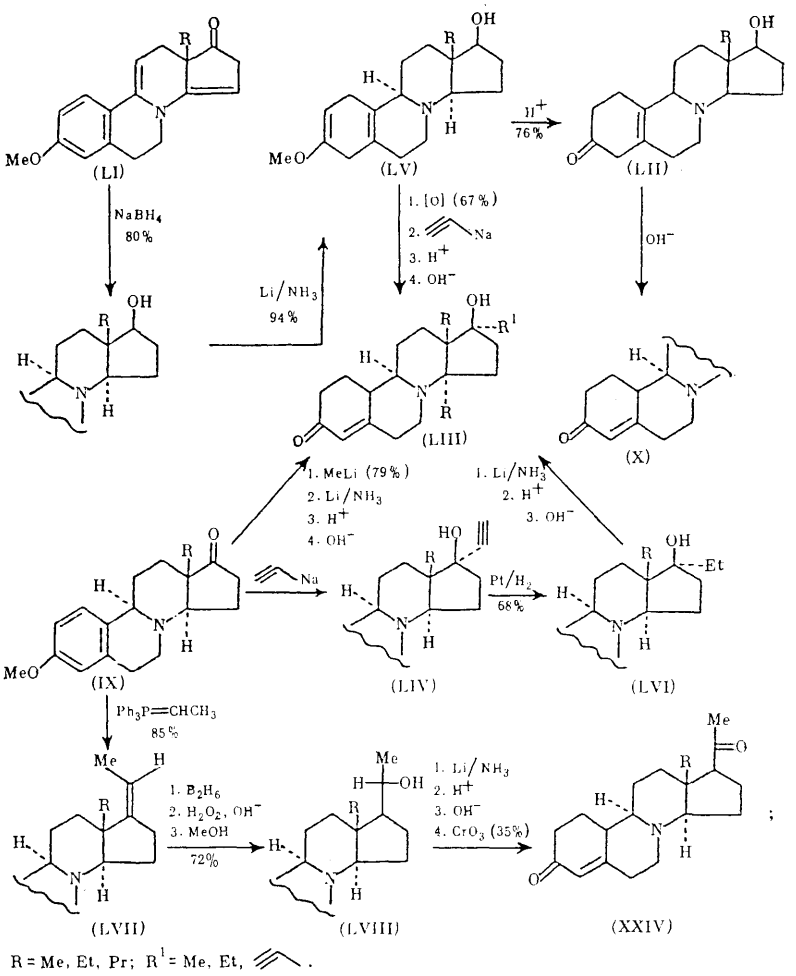


A simple scheme for the synthesis of 12-oxo-derivatives of 8-azasteroids consists in the condensation of 3,4-dihydroisoquinolines (LIX) with 2-acetylcycloalkanones (LX) (Scheme 8).[31] The enaminoketones (LXI) are then formed in yields ranging from 7 to 85%. Some of them had been obtained earlier (Z = CH_2).[16] The condensation of 6,7-dimethoxy-3,4-dihydroisoquinoline (LIX) with 2-acetyldimedone (LXII) yielded the enaminodiketone (LXIII). The attempt to condense the non-enolysable β-diketones (LXIV) with an angular substituent leads to the opening of the β-diketone ring and subsequent alkylation and acylation of the dihydroisoquinoline at C(1) and N respectively. This entails the formation of azecinotetrahydroisoquinolines (LXV) and *N*-acetyl-1-(2-oxocycloalkyl)tetrahydroisoquinolines (LXVI).[32]

Synthesis of 18-nor-8-azasteroids[33], which differs from Meltzer's method[5] by the procedure used to obtain the unsaturated lactams (LXVII) (Scheme 9), was proposed in 1975. The cyclisation of these lactams under the influence of polyphosphoric acid (PPA) is accompanied by oxidative-reductive disproportionation and takes place quantitatively to give an equimolar mixture of the immonium salts (LXVIII) and the pyridinium salts (LXIX). Treatment of the salt (LXVIII) with a base gives rise to the enaminoketone (XLVII), which is reduced with lithium tetrahydroaluminate (when $R=R^1=OCH_3$) to a derivative of 18-nor-8-azaoestrone (XLIX) having the *syn,trans,cis*-configuration. The attempts to introduce an angular substituent in the 13-position of the enaminoketone (XLVII) were unsuccessful and only the *O*-alkylation product was isolated in the form of the immonium salt. Its reduction with tetrahydroborate yielded a mixture of the bases (LXX) and (LXXI).

The synthesis of 12-oxo-derivatives of 8-azasteroids (XXXVIII) by the reaction of the hydrochloride of 3,4-dihydroisoquinoline (LIX) with αβ-unsaturated ketones (LXXII)

Scheme 7

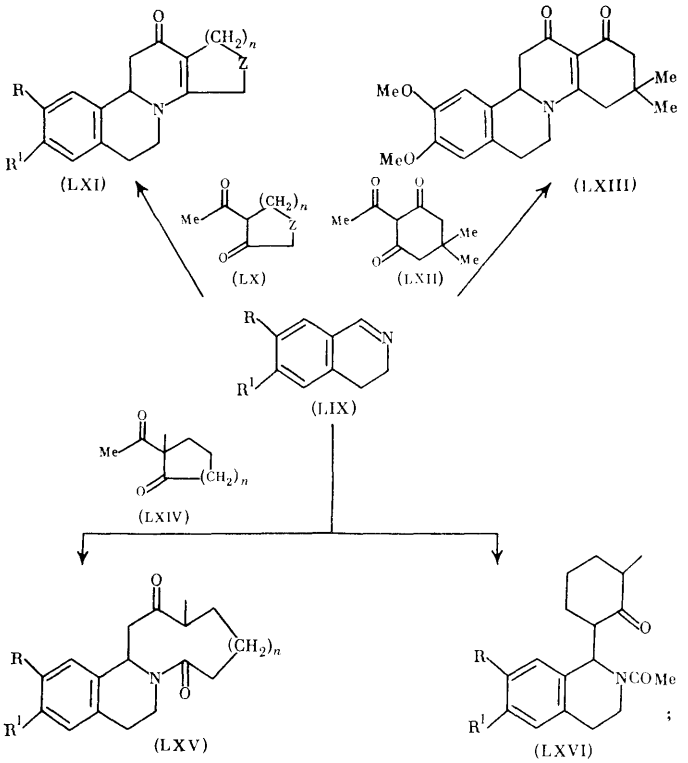


was achieved independently by two groups of investigators (Scheme 10).[34-41] The compounds are formed in the form of a mixture of two or three isomers with respect to C(9) and C(13) and the isomeric composition depends on the reaction conditions and the size of the ring in the αβ-unsaturated ketones (LXXII).[36-38] The configuration of the compounds obtained was investigated chemically by the interconversion of various epimers and oxidation to the enaminoketone (LXXIII) by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and to the γ-pyridone (LXXIV) in the presence of mercury diacetate[36,39]. 12-Hydroxyimino-derivatives of type (LXXV) with different substituents in the 2-, 3-, 4-, 7-, and 11-positions[34] were obtained and a study was made of the elimination of the 12-carbonyl group by various reducing agents[40]. The stereochemistry of the resulting compounds with a six-membered D ring was partly confirmed by ^1H and ^{13}C NMR data[41].

The first study of the synthesis of 8-azasteroids in the USSR was published in 1969 [42] (Scheme 11). The key stage is the reaction of triacylmethanes (LXII) with 3,4-dihydroisoquinolines (LIX). This leads to the formation of the enaminodiketones (LXIII), which have the 8-azasteroid skeleton[42-44]. The enaminodiketone group in compound (LXIII) proved to be chemically extremely inert. The attempts to introduce the angular methyl group in the 13-position were unsuccessful: under the severe conditions of the anionoid *C*-methylation, it was possible to isolate only the 16-methyl derivative in an insignificant yield[44]. We were able to achieve the selective removal of the 12-oxo-group from the enaminodiketones (LXIII) under the conditions of the ionic hydrogenation reaction. The reaction proceeds with total regiospecificity giving rise to products having the general formula (XLVII) in a high yield[45]. It was found that the Baeyer–Villiger oxidation of the enaminodiketones (LXIII, $Z=CH_3$) leads to the formation of the ε-lactones (LXXVI), whose methanolysis results in the formation of the diketoesters (LXXVII), which exist in equilibrium with the keto-enol form.

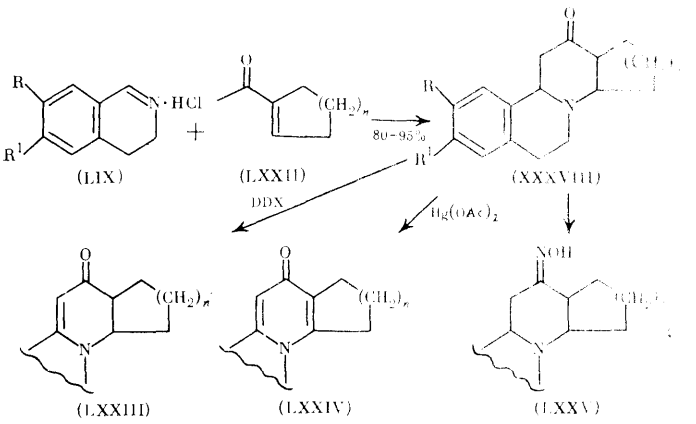
The cyclodehydrogenation of the diketoester (LXXVII) proceeds with simultaneous dehydrogenation to give the benzopyrrocolines (LXXVIII).[46,47] The dehydrogenation of the enaminodiketones (LXIII) leads to the formation of the γ-pyridones (LXXIX),[48] the polyfunctional group of which proved to be more reactive. Thus the ionic hydrogenation of the pyridones (LXXIX) proceeds with hydrogenolysis of the keto-group in the D ring to form the 17(17a)-deoxo-compounds (LXXIV) with a satisfactory yield[49]. A method was therefore developed for the direct synthesis of γ-pyridones by the condensation of 3,4-dihydroisoquinoline *N*-oxide (LXXX) with triacylmethanes (LXII).[47,48,50] The condensation proceeds via the 1,3-addition with subsequent cyclodehydration of the intermediate β-triketone. The presence

Scheme 8



R, R^1 = H, OMe; Z = CH_2, NH, $NCOC_6H_5$; n = 1, 2, 3 .

Scheme 10

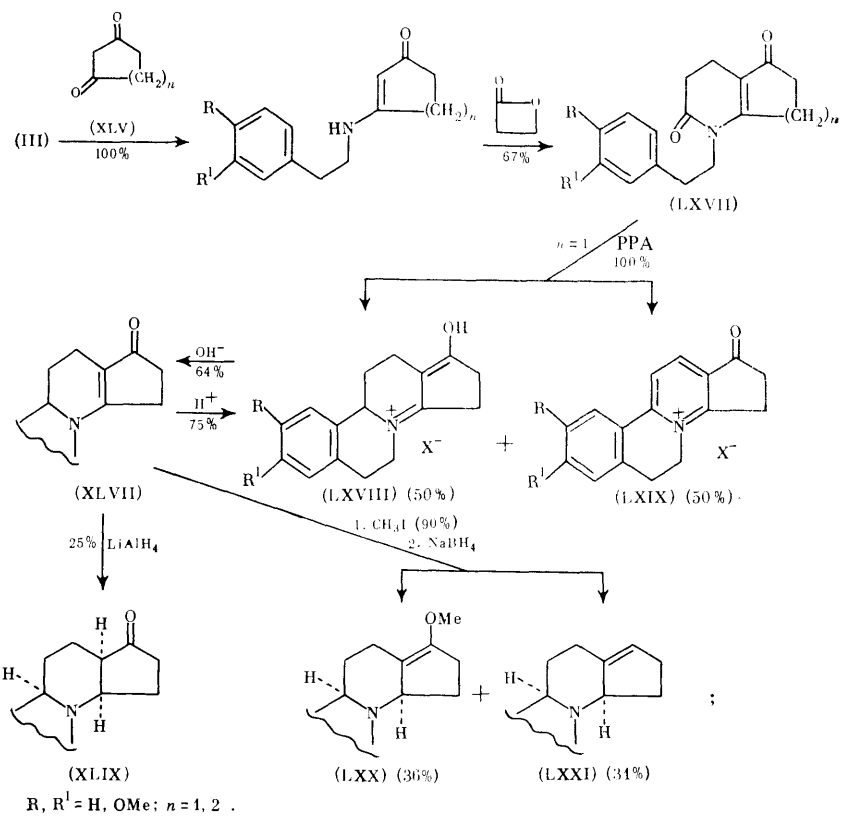


R, R^1 = H, OMe, F; n = 1, 2 .

of the $\Delta^{9(11)}$-bond destabilises the enaminodiketone group and the pyridone (LXXIX) reacts with allyl bromide to form a pyridonium salt, which is reduced, without further purification, to the dihydropyridone (LXXXI) with zinc and acetic acid.

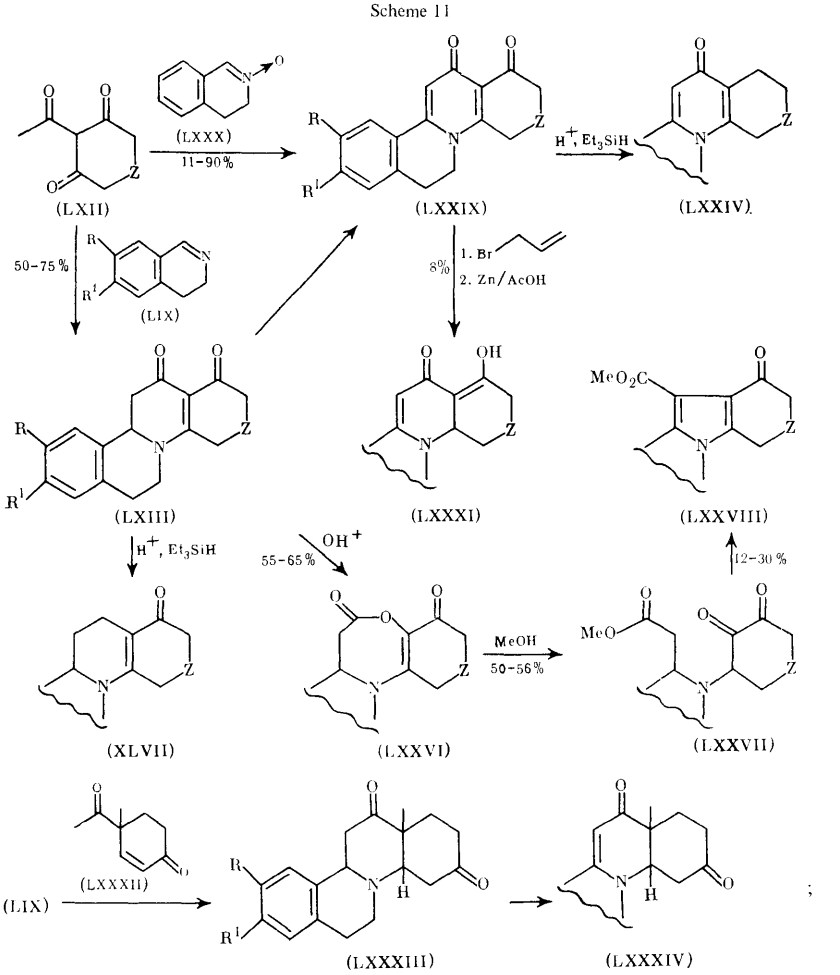
The condensation of 3,4-dihydroisoquinolines (LIX) with the diketone (LXXXII) results in the formation of the 8-aza steroid compounds (LXXXIII) with a *cis*-C/D-junction[51,52]. The dehydrogenation of the latter by chloranil leads to the formation of the enaminoketones (LXXXIV). The reduction of compounds (LXXXIII) and (LXXXIV) as well as their tosylhydrazones by sodium tetrahydroborate has been studied[53].

Scheme 9



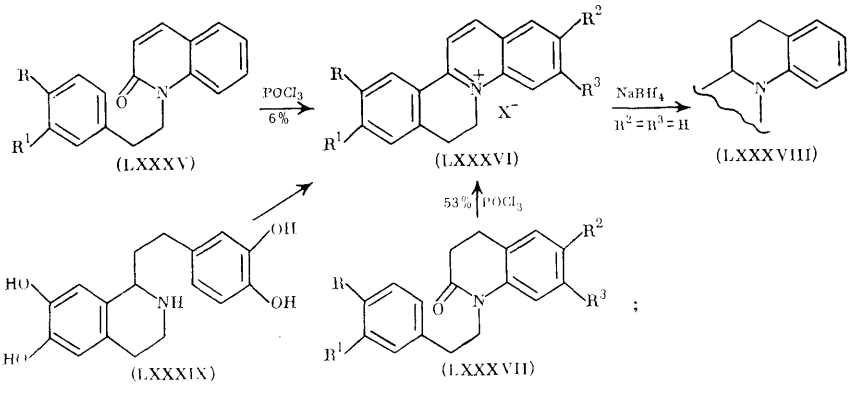
R, R^1 = H, OMe; n = 1, 2 .

Scheme 11



R, R^1 = H, OMe; Z = —, CH_2, $CHCH_3$, $C(CH_3)_2$, CHC_6H_5 .

Scheme 12



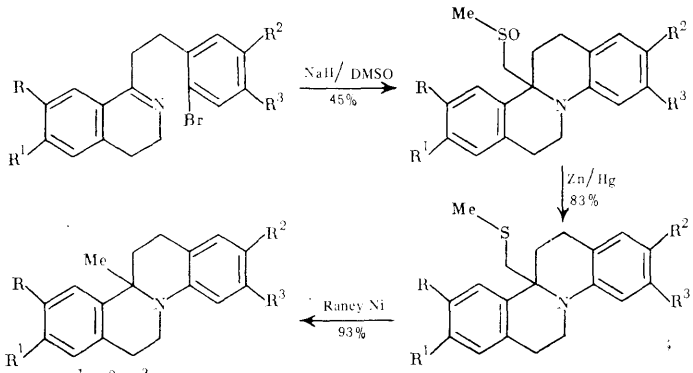
R, R^1 = OMe, —O—CH_2—O—; R^2, R^3 = H, OMe; X = Cl, I .

III. COMPOUNDS WITH TWO AND MORE AROMATIC RINGS

Polycyclic compounds with two and more aromatic rings, which formally have the 8-azasteroid skeleton, were obtained even before the initiation of studies on the total synthesis of 8-azasteroids. Various modern reduction methods make it possible to convert these compounds into compounds with saturated B, C, and D rings. Brown's studies[54] on the synthesis of dibenzo[*a*,*f*]quinolizines, in which the incorrect conclusions concerning the structure reached in analogous investigations by Japanese workers[55] were corrected, are characteristic in this respect. Thus the cyclisation of the amide (LXXXV) yielded a mixture of quaternary salts having various structures, from which dibenzo[*a*,*f*]quinolizinium iodide (LXXXVI) was isolated (Scheme 12).

The same product is formed on cyclisation of the dihydroquinoline (LXXXVII).[56] The reduction of the tetracyclic salt (LXXXVI) with tetrahydroborate gives rise to the dibenzo[*a*,*f*]quinolizine (LXXXVIII). Analogous data were obtained for the cyclisation of the dihydroquinolone (LXXXVII) [56] or the tetrahydroisoquinoline (LXXXIX) [57] with subsequent *O*-methylation. The synthesis of angularly substituted dibenzo[*a*,*f*]quinolizines has been achieved in accordance with Scheme 13:[58–60]

Scheme 13



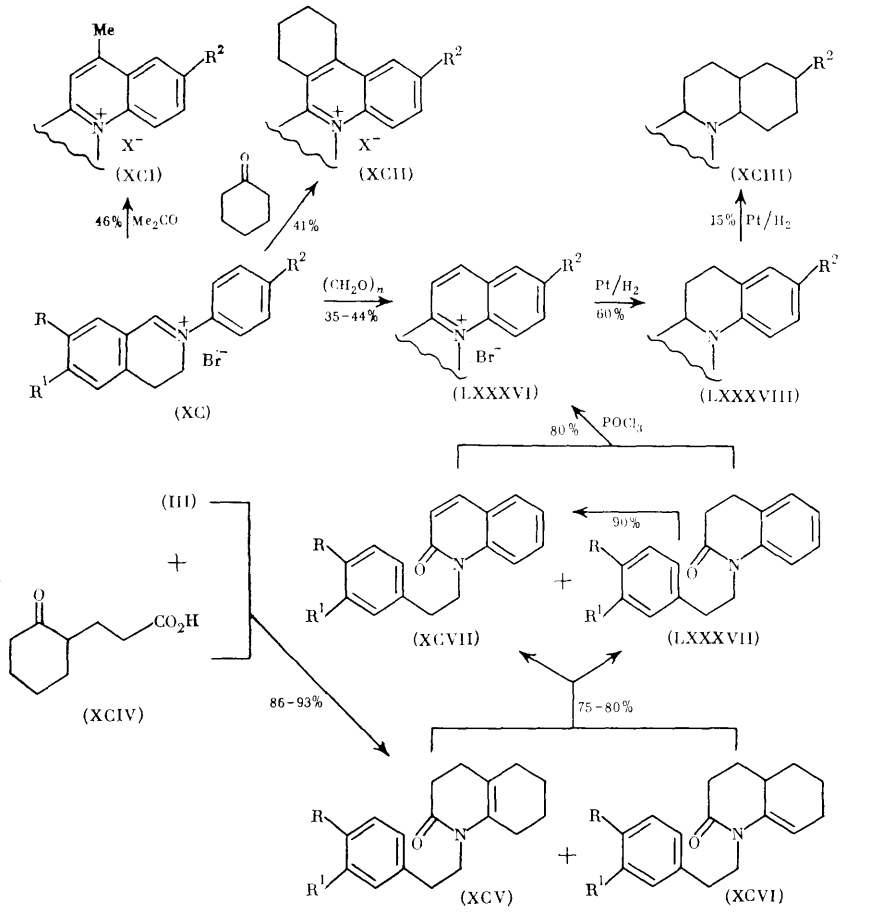
R, R^1, R^2, R^3 = H, OAlk, OH, —O—CH_2—O—, Alk .

Salsmans and Van Binst[61] developed a method of synthesis of compounds containing the tetracyclic 8-azasteroid skeleton (Scheme 14) on the basis of the reaction of 2-phenyl-3,4-dihydroisoquinolinium salts (XC) with carbonyl compounds. The proposed mechanism of the formation of compounds (LXXXVI), (XCI), and (XCII) involves the Michael addition of CH-active compounds to the C=N bond with subsequent stages involving the intramolecular electrophilic attack by the carbonium ion on the activated *ortho*-position of the *N*-aryl substituent, the elimination of water, and intramolecular hydride transfer. The catalytic hydrogenation of the isoquinolinium salts (LXXXVI) yields dibenzo[*a*,*f*]quinolizines (LXXXVIII), which are converted by more far-reaching reduction into the D-homo-8-azasteroid derivatives (XCIII), whose configuration has not been established.

Later an improved synthesis of dibenzo[*a*,*f*]quinolizines (LXXXVIII) was described[62]. A mixture of enamides (XCV) and (XCVI), with the former predominating, was obtained by the condensation of β-phenylethylamines with the acids (XCIV) (Scheme 14). The dehydrogenation of this mixture yielded compounds (XCVII) and (LXXXVII), whose cyclisation gave rise to the quinolizinium salt (LXXXVI, R=R^1=OCH_3). Derivatives unsubstituted in the A ring are not cyclised.

The synthesis of 8-azasteroid compounds with an 11-12-condensed E ring has been achieved by the same group of investigators[63] (Scheme 15). The interaction of the aldehyde

Scheme 14



R, R^1, R^2 = H, OMe; X = Cl, Br, ClO_4 .

(XCVIII) with 2-phenylcyclohexylamine (XCIX, $n = 2$) yielded the *trans*- or *cis*-dihydroisoquinolinium salt (C), depending on the stereochemistry of the initial phenylcyclohexylamine. The cyclisation of this salt under the influence of polyphosphoric acid gives rise to the corresponding *trans*-C/D- and *cis*-C/D-dibenzo[*a*,*f*]-quinolizines (CI). Other stereoisomeric bases (CI) have been obtained from β-phenylethylchloride (CII) and benzonitrile (CIII), as shown in the Scheme. The stereochemistry of all the bases (CI) obtained was established on the basis on ^1H and ^{13}C NMR data[64] and by comparison with the spectroscopic characteristics of model compounds[65,66].

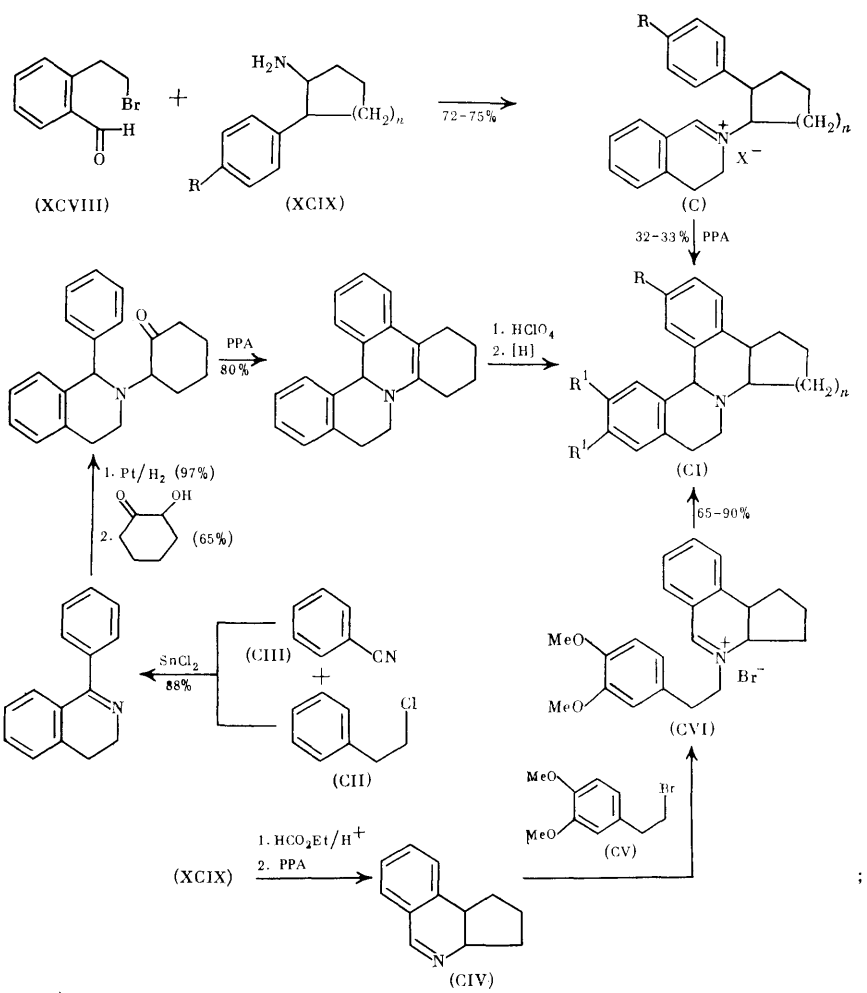
The use of 2-phenylcyclopentylamines (XCIX, $n = 1$) in the reaction with the aldehyde (XCVIII) makes it possible to obtain 8-azasteroid compounds (CI, $n = 1$) with a five-membered D ring[67]. An alternative pathway leading to the formation of compounds (CI, $n = 1$) was proposed by the same workers. Refluxing of the amine (XCIX) in ethyl formate with subsequent cyclisation of the formamide results in the formation of the dihydroisoquinoline (CIV), which leads to the immonium derivative (CVI) on heating with the bromide (CV). Cyclisation of the immonium derivative gives rise to the pentacyclic product (CI). The pathways leading to the cyclisation of compounds (CVI) to (CI) and the causes of the formation of various isomers as a function of the stereochemistry of the initial amine (XCIX) and the selected synthetic scheme have been investigated.

The tribenzoquinolizine analogues of 8-azasteroids (CIX) have been obtained by condensing the aldehyde (XCVIII) with 2-aminobiphenyl (CVII) (Scheme 16)[68] and subsequent acid or photochemical cyclisation to the phenanthridizinium salt (CVIII) and its reduction without isolation in a pure form. Analogous products have been obtained from tetrahydroisoquinolines (CX):[69]

In the course of studies of the methods of synthesis of compounds containing the dibenzoquinolizinium cation in order to obtain precursors of 8-azasteroids, a method has been developed for the synthesis of dibenzo[*a*,*f*]quinolizinium perchlorates (CXIII) (Scheme 17) by the condensation of the isoquinolines (CXI) with the aldehydes (CXII) and subsequent intramolecular cyclisation[70]. The application of this method to the synthesis of 17-nitro-substituted precursors of D-homo-8-azasteroids made it possible to synthesise various tetracyclic compounds (CXIII) containing the OH, OAc, and OMe groups in the A ring and the NO_2 group in the D ring[71]. The use of the dihydroisoquinolines (CXIV) in this sequence of reactions leads initially to the heterocyclic diene (CXV), which subsequently cyclises quantitatively to the tetracyclic 17-nitro-derivative (CXVI):

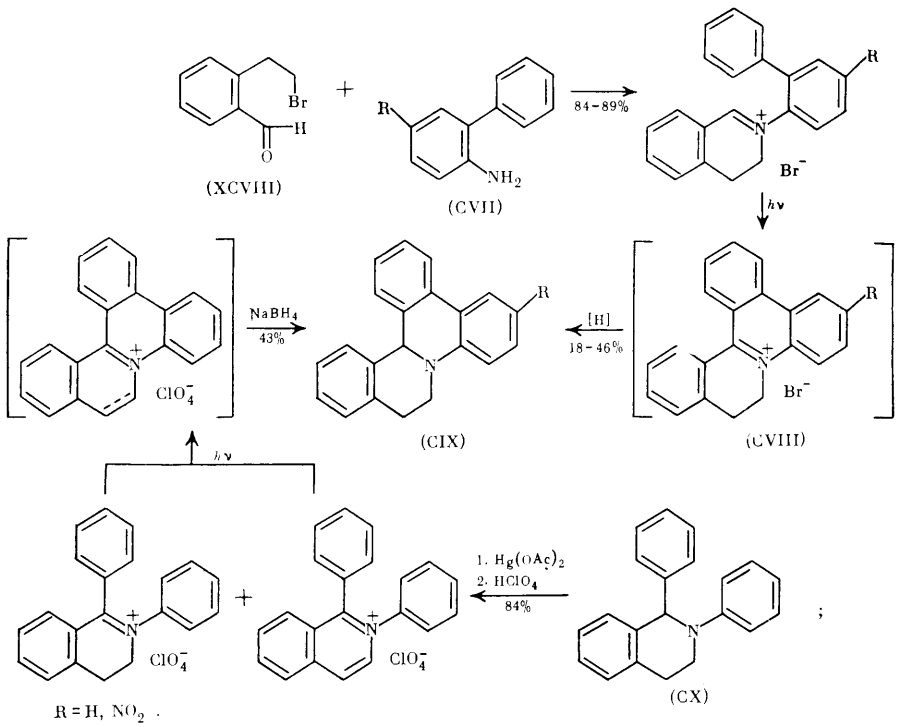
In 1975 Chapman[72] obtained the quinolizinium perchlorates (CXVIII) and (CXX) (Scheme 18) by the condensation of 3,4-dihydroisoquinolinium perchlorate (LIX) with the cyclic αβ-unsaturated ketones (CXVII) and (CXIX) containing a methyl substituent in the β-position.

Scheme 15

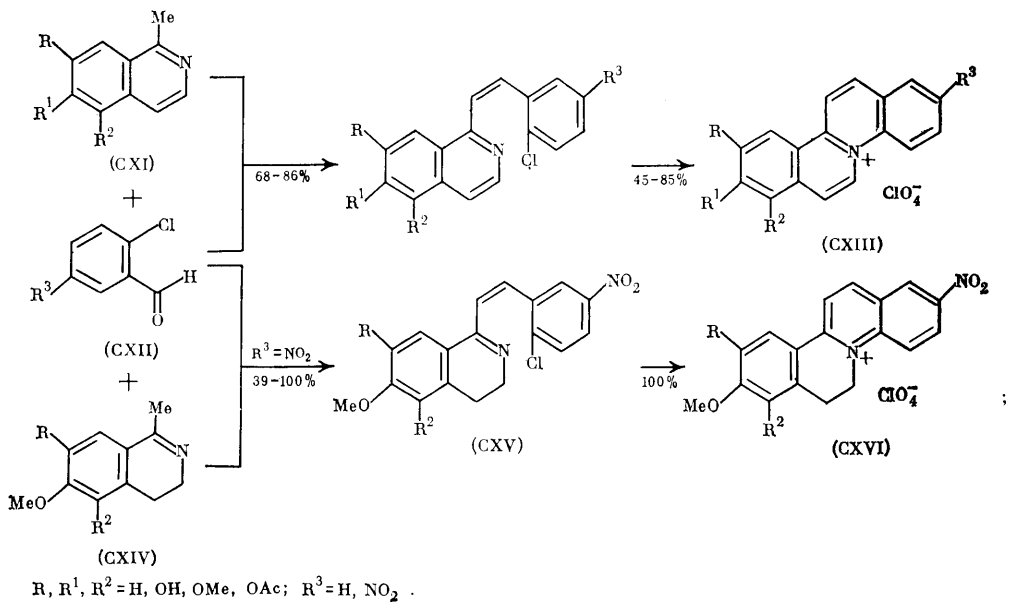


R, R^1 = H, OMe; n = 1, 2 .

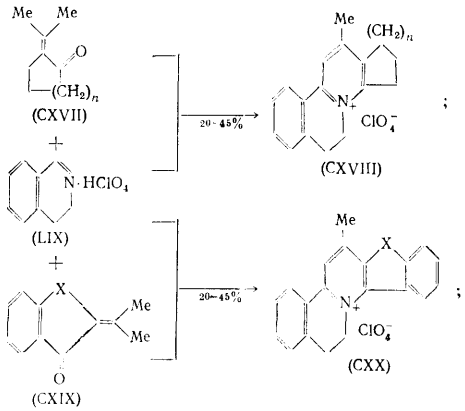
Scheme 16



Scheme 17



Scheme 18

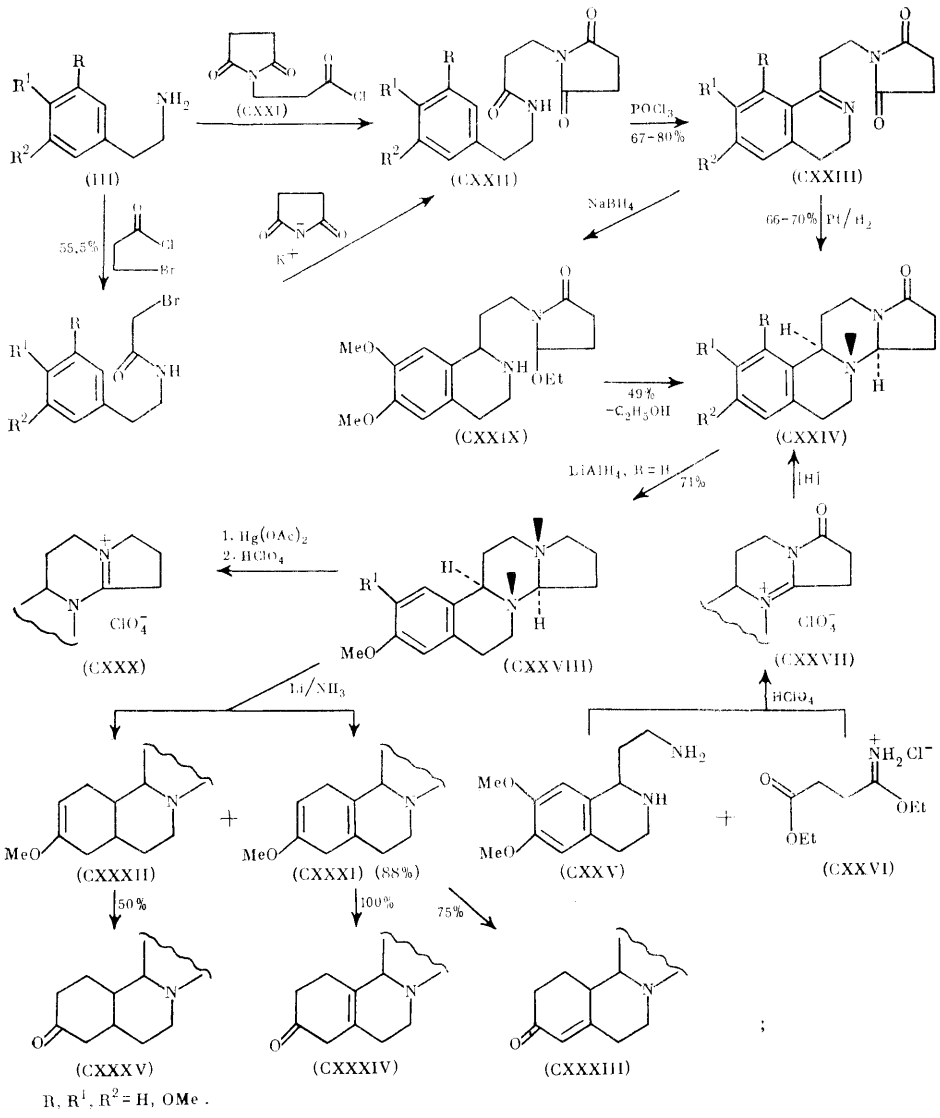


$n = 1, 2$, X = CH_2, O, SO_2 .

IV. COMPOUNDS WITH AN ADDITIONAL HETEROATOM

The synthesis of 8-azasteroid compounds with an additional heteroatom can be achieved with the aid of the approaches described in Section II and also by special methods. Thus Scheme 19 illustrates different ways of constructing the 8,13-diazasteroid molecule from β-phenylethylamines (III). Thus the interaction of compounds (III) and the acid chloride (CXXI) gives rise to the amide (CXXII), which cyclises to the dihydroisoquinoline (CXXIII).[73] Its subsequent reductive cyclisation results in the formation of 8,13-diazaoestrane derivatives (CXXIV). It was found that the failure of the attempt at reductive cyclisation described by Burckhalter and Abramson[74] was associated with the use of the dihydroisoquinoline (CXXIII) in the form of the hydrochloride, as pointed out by Taylor and Lenard[73]. This entails reductive cleavage, leading to the diamine (CXXV) whose interaction with the hydrochloride (CXXVI) leads to a derivative of 8,13-diazagonane (CXXVII).[74] The reduction of the immonium linkage with various reagents results in the

Scheme 19



R, R^1, R^2 = H, OMe .

formation of the diazasteroid (CXXIV),[75] which give rise to the diamines (CXXVIII) on treatment with lithium tetrahydroaluminate. X-Ray diffraction studies of the amide (CXXIV)[75] and also infrared and ^{1}H NMR spectroscopic data[79] showed that compounds (CXXIV) and (CXXVIII) have the 9α,14α-configuration with the *trans*-B/C- and *trans*-C/D-junctions.

The fragmentation and possible pathways leading to the decomposition of compounds (CXXIII) and (CXXVIII) under mass-spectrometric conditions have been studied[77].

Another version of the synthesis of the amide (CXXII) consists in the condensation of the β-phenylethylamines (III) with 3-bromopropionyl bromide and the reaction of the resulting bromamide with the potassium derivative of succinimide[78]. The tetrahydroisoquinoline (CXXIX), which gives rise to the 8,13-diazasteroid (CXXIV) after the azeotropic distillation of the alcohol, has been obtained in the study of the reductive cyclisation of the dihydroisoquinoline (CXXIII) under the influence of sodium tetrahydroborate[79]. The removal of the keto-group followed by oxidation with mercury acetate leads to the immonium salt (CXXX), in which the presence of the $\Delta^{13(14)}$-bond has been demonstrated by ultraviolet spectroscopy.

The Birch reduction of 8,13-diazasteroids (CXXVIII) has been investigated. The main reduction product is the diene (CXXXI), which is converted either into the non-conjugated enone (CXXXIV) or into 8,13-diaza-19-norandrost-4-en-3-one (CXXXIII) depending on the conditions used in the treatment. The enolic ether (CXXXII), formed in the course of their reduction, gives rise to 8,13-diaza-19-norandrostan-3-one (CXXXV) as a result of appropriate treatment. ^{13}C NMR data have been published for compounds (CXXXI) and (CXXXII)[80] and also for compounds (CXXIII), (CXXIV), and (CXXVIII).[81]

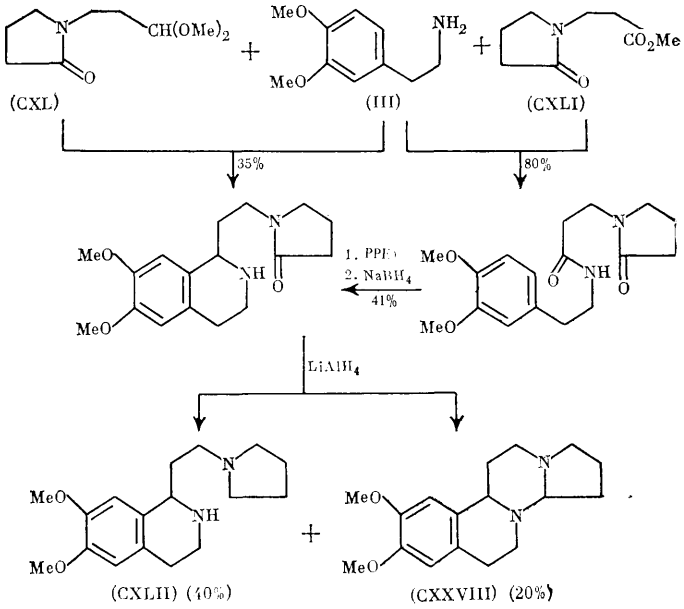
The attempts at the synthesis of C-nor-, C-homo-, and D-homo-8,13-diazaoestranes in accordance with the scheme examined above with the appropriate replacement of the starting compound were unsuccesful[76].

The use of potassium phthalimide in condensation with the bromamide (CXXXVI) leads to the formation of the amide (CXXXVII),[82] whose cyclisation produces the dihydroisoquinoline (CXXXVIII) (Scheme 20). The reductive cyclisation of the latter proceeds via an intermediate tetrahydroisoquinoline to form the diazasteroid (CXXXIX) containing the additional saturated E ring. In order to retain the aromtic E ring, the reductive cyclisation is carried out with sodium tetrahydroborate. In the study of the configuration of compound (CXXXIX) considerable difficulties arose as a consequence of the presence of the additional D/E-junction.

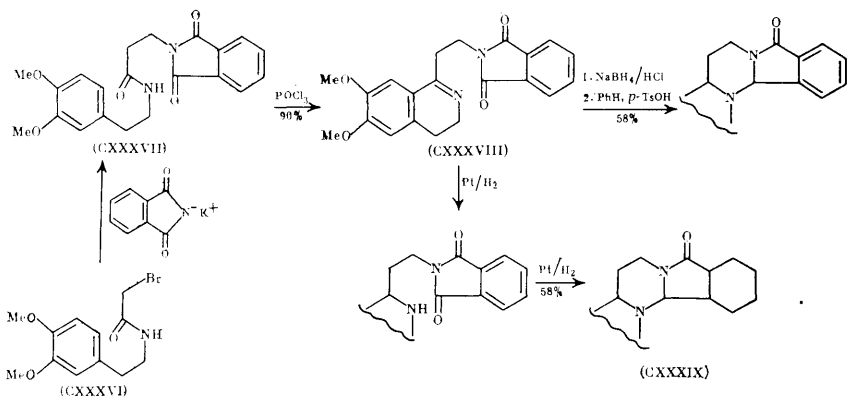
Infrared and ^{1}H NMR spectroscopic data make it possible to postulate the *trans*-C/D-junction and the *syn*-H(9)/H(14)-configuration. However, the constant $J_{H(14)/H(15)} = 4$ Hz precludes a choice between the *trans*- and *cis*-D/E junctions. X-Ray diffraction analysis demonstrated the α-orientation of the H(14), H(15), and H(16) protons, which indicate a *cis*-D/E-junction.

The synthesis of 8,13-diazasteroids was undertaken on the basis of the condensation of homoveratrylamine (III) with the acetal-lactam (CXL) or with the ether-lactam (CXLI), the closure of the C ring being achieved by reductive annelation under the influence of lithium tetrahydroaluminate[83] (Scheme 21). The 8,13-*seco*-diazasteroid (CXLII) is then formed as a side product. From infrared and ^{1}H NMR spectroscopic data a *trans*-B/C-junction and the *syn*-orientation of the H(9) and H(14) protons were attributed to the 8,13-diazasteroid (CXXVIII).

Scheme 21

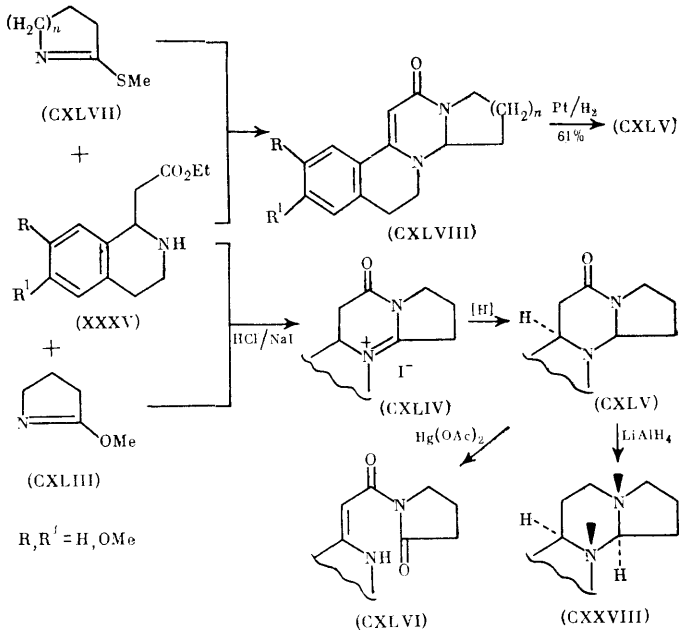


Scheme 20



Japanese chemists proposed[84,85] another approach to the synthesis of 8,13-diazasteroids (Scheme 22) on the basis of the reaction of the tetrahydroisoquinoline ester (XXXV) with the butyrolactam (CXLIII), which proceeds with formation of an unstable tetracyclic compound, which gives rise to the salt (CXLIV) on treatment with HCl/NaI. On reduction, this salt is converted into a mixture of the two isomeric bases (CXLV). The *trans*-B/C-junction with the *syn*-orientation of H(9) and H(14) and the *cis*-B/C-junction with the *anti*-orientation of these protons were attributed to the bases[85]. The reduction of the aminoketones (CXLV) or of the salt (CXLIV) with lithium tetrahydroaluminate leads to a 70% yield [relative to compound (XXXV)] of the diamine (CXXVIII), which has the same configuration as the compound obtained earlier[74]. The attempt to oxidise the base (CXLV) with mercury acetate to the corresponding $\Delta^{9(11)}$-derivative gives rise to the cleavage product (CXLVI) only.

Scheme 22



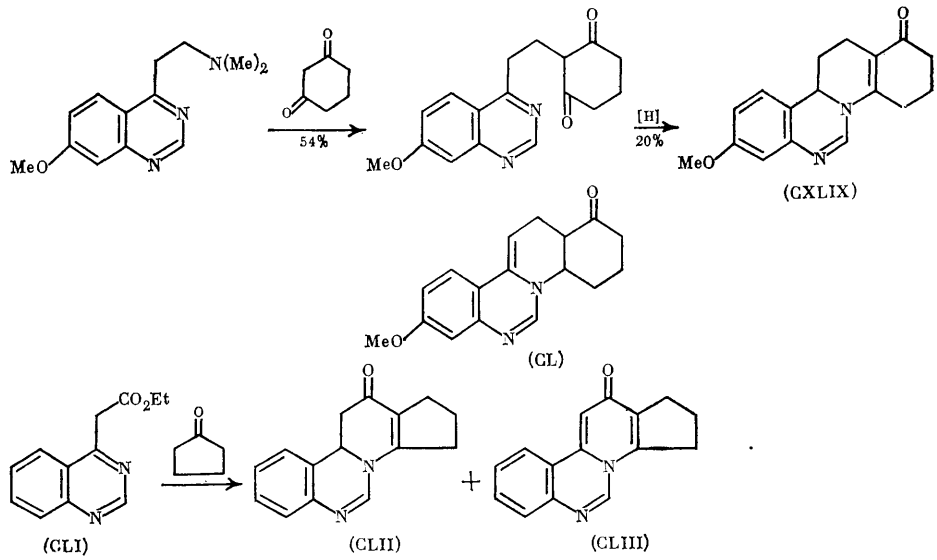
Using the lactim thioethers (CXLVII) in the condensation with the ester (XXXV), 8,13-diazasteroids (CXLVIII) were also obtained in yields of 63% ($n = 1$), 81% ($n = 2$), and 7.8% ($n = 3$).[86] The reduction of compound (CXLVIII, $n = 1$) over the Adams catalyst yields the 8,13-diazasteroid (CXLV).

The synthesis of 6,8-diazasteroid systems was undertaken in 1964 [87] by a method analogous to that of Clarkson[28], as shown in Scheme 23. The ^{1}H NMR spectrum of compound (CXLIX) in trifluoroacetic acid contains a signal at 4.86 p.p.m., which the author attributed to the olefinic protons, which he believes to arise as a consequence of the isomerisation of the initial compound in an acid medium to the enamine (CL). Such isomerisation is unlikely, particularly since, according to our data[44], the signal at 4.86 p.p.m. in trifluoroacetic acid can be quite legitimately assigned to the benzyl H(9) proton of the base (CXLIX).

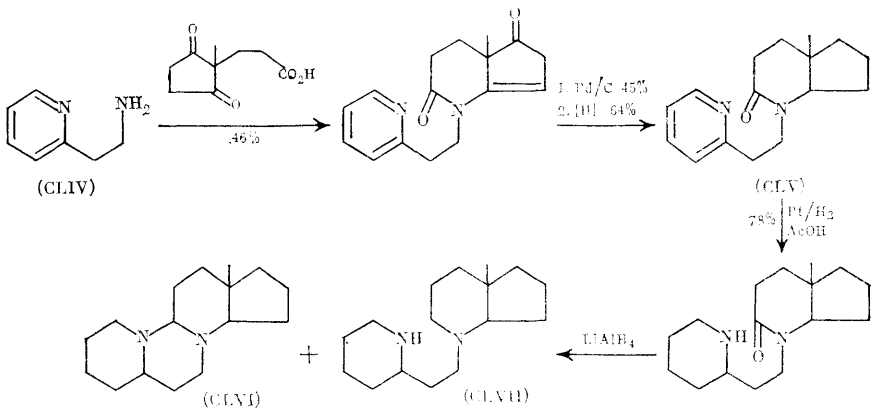
The attempt to synthesise 6,8-diazasteroid systems by the condensation of ethyl 3,4-dihydro-4-quinazolinylacetate (CLI) with cyclopentanone was unsuccessful[88] (Scheme 23). The authors were able to isolate only traces of compounds to which the structures (CLII) and (CLIII) were attributed on the basis of infrared spectroscopic and mass-spectrometric data.

The synthesis of 8,10-diazasteroids was undertaken by a group of Japanese chemists by a method[89] (Scheme 24) analogous to that of Brown et al.[6] The use of the pyridine derivative (CLIV) made it possible to obtain a ketolactam, which was reduced to the amide (CLV) via a thioketal with subsequent desulphurisation. The saturation of the pyridine ring and subsequent reductive cyclisation give rise to a mixture of two isomers of the 8,10-diazasteriod (CLVI) and the non-cyclised product (CLVII) in yields of 16, 21, and 32% respectively. Compounds (CLVI) are stereoisomers with respect to the C/D-junction. The stereochemistry of the final product was established on the basis of the postulated mechanism with reductive cyclisation and also infrared and ^{1}H NMR spectroscopic data. The physicochemical criteria of the stereochemistry of the compounds presented by Takahata et al.[89] are not unduly convincing, since the stereochemistry of the proton at C(9) is assessed from the presence of the Boltzmann bands in the infrared spectrum, which in the given instance can be accounted for also by a *trans*-diaxial disposition of the hydrogen atom at C(5) and the free electron pair of the N(10) nitrogen atom, while the ^{1}H NMR criteria, in

Scheme 23



Scheme 24



terms of which the stereochemistry of the proton at C(9) is usually deduced from its chemical shift, refer to the tetrahydroisoquinoline fragments and their *a priori* employment in the given instance is unjustified.

8,11-Diazasteroid compounds have been synthesised in accordance with Scheme 25.[90] The addition of homoveratrylamine to 1-cyanocyclopentene (CLVIII) yields the aminonitrile (CLIX) in the form of a mixture of the *cis*- and *trans*-isomers. Their interaction with chloroformic ester results in the formation of a mixture of the urethanes (CLX) and (CLXI) in proportions of 5 : 1, the latter isomerising to the former on treatment with sodium ethoxide. The *cis*- and *trans*-configurations were attributed to the compounds on the basis of the hypothesis that the *trans*-isomer is thermodynamically more stable. The hydrogenation of the *trans*-nitrile (CLX) over Raney nickel leads to the corresponding amine (CLXII), whose heating at 170 °C in ethylene glycol gives rise to the pyrimidinone derivatives (CLXIII) with a *trans*-C/D-junction. The cyclisation of compounds (CLXIII) and (CLXIV) leads to the hydrochlorides of the 8,11-diazasteroids (CLXV) and (CLXVI) respectively. In the case of the derivative (CLXIII), the main reaction product is then the chloro-compound (CLXVII). Treatment of the salts (CLXV) and (CLXVI) with alkali gives rise to the free bases (CLXVIII) and (CLXIX) with a low overall yield.

Meyers' method (see Scheme 5) has been used to synthesise 8,16- and 8,17-diazasteroids[91] (Scheme 26). The initial compounds in this Scheme are trimethylpyrrolidinone (CLXX) and *N*-acetylpyrrolidinone (CLXXI), which were condensed with the ester (XXXV). This led to the formation of the enaminoketones (CLXXII) in the former case and the isomeric *N*-acetyl derivatives (CLXXIII) and (CLXXIV) in the latter case. The structures of the diazasteroids (CLXXIII) and (CLXXIV) were established on the basis of the ultraviolet and ^{1}H NMR spectra and also by a comparative study of their fragmentation in the mass spectra.

A novel scheme has been proposed for the synthesis of 8,14-diazasteroids[92] (Scheme 27). Compound (CLXXV) was obtained by the sequence of reactions presented in the Scheme. The subsequent synthesis is carried out via two equally important pathways. The first postulates the cyclisation of compound (CLXXV) and the catalytic hydrogenation of the intermediate salt (CLXXVI). The tricyclic ester (CLXXVII) formed under these conditions is converted into the 8,14-diazasteroid (CLXXVIII) on refluxing in ethylene glycol. In the second method the D ring is formed initially by refluxing the ester (CLXXV) in ethylene glycol and the resulting amide (CLXXIX) is cyclised to the $\Delta^{9(11)}$-8,14-diazasteroid (CLXXX). Its conversion into the iodonium salt and reduction with sodium tetrahydroborate or catalytically give rise to the diazasteroid (CLXXVIII), to which the *cis*-quinolizidine structure was attributed from infrared and ^{1}H NMR spectroscopic data and the results of the selective deuteration in the 9-position, and also bearing in mind its resistance to oxidation to the dehydro-derivative (CLXXX) on treatment with mercury acetate. The mutual orientation of the H(9) and H(13) protons was not established.

The synthesis of 8,15-diazasteroids was undertaken by the method of Yamazaki et al.[93] (Scheme 28), which is analogous to the method of Meltzer et al.[5] The condensation of homoveratrylamine with the pyrrolidinone derivatives (CLXXXI) yielded the amide (CLXXXII), whose cyclisation under the influence of ethyl polyphosphate (PPE) gives rise to the dihydroisoquinoline (CLXXXIII). The reductive cyclisation of the latter leads to a mixture of the non-cyclised product (CLXXXIV) and the 8,15-diazasteroid (CLXXXV). The *anti*,*trans*,*trans*-configuration has been attributed to compound (CLXXXV).

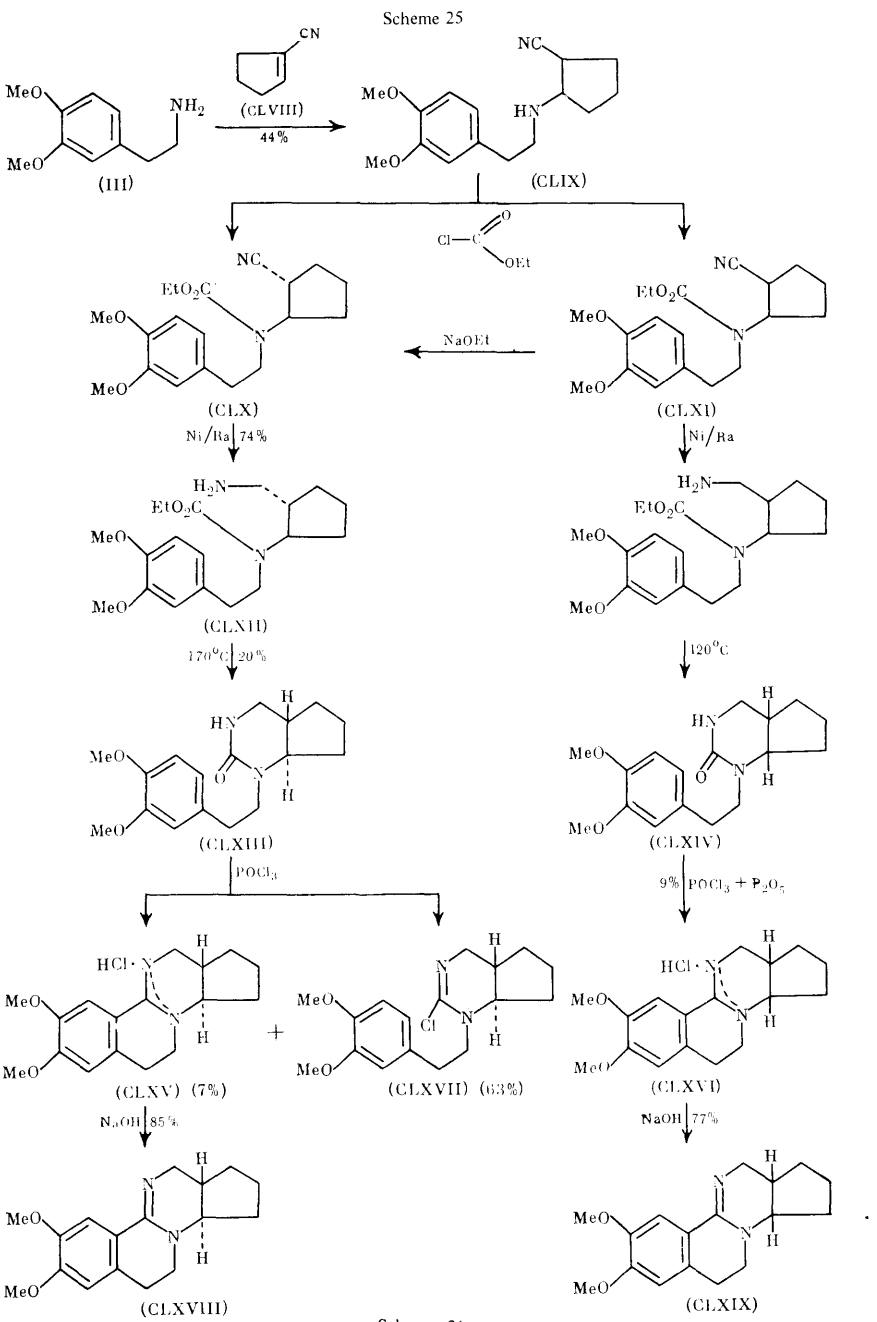
In the search for new biologically active compounds in the series of 8-azasteroid derivatives with an additional heteroatom, the synthesis of D-homo-8-aza-17-thia- and D-homo-8,17-diaza-steroids was undertaken[94] (Scheme 29). For this purpose, the ester (XXXV) was condensed with the heterocyclic ketones (CLXXXVI) and (CLXXXVII) to form the tetracyclic enaminoketones (CLXXXVIII) and (CLXXXIX). The introduction of the 3-tetralone (CXC) into this condensation gives rise to the D-homo-8-azasteroid (CXCI) with the additional aromatic E ring.

The synthesis of 8,12-diaza-D-homosteroids was undertaken by a group of Japanese investigators[95] (Scheme 29) in order to study their biological activity. The tetracyclic diene (CXCIII) was obtained by the condensation of the amine (CXXV) with cyclohexane-1,2-dione (CXCII) and was converted by reduction over the Adams catalyst and subsequent acylation into the 8,12-diaza-D-homosteroid (CXCIV) as a mixture of two isomers with respect to C(9), the *trans*-B/C-isomer being isolated in 22% yield and the *cis*-B/C-isomer in 9% yield. The stereochemistry of the compounds obtained was established from infrared and ^{1}H NMR spectroscopic data and was confirmed by studying the rates of oxidation to the corresponding $\Delta^{9(11)}$-derivatives.

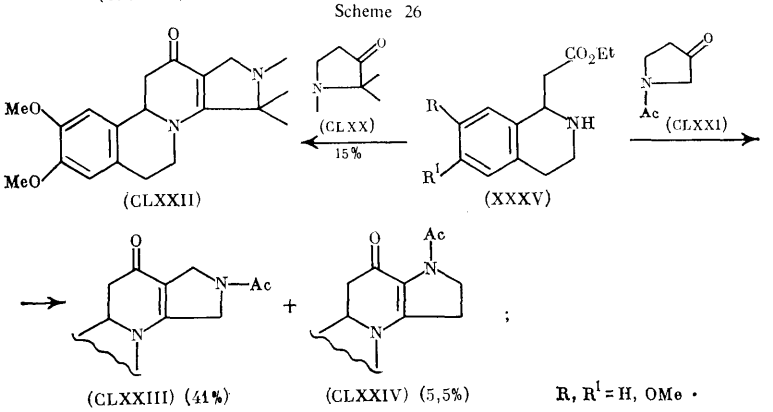
4,8-Diazasteroids (CXCV) were obtained in 1979 by the method illustrated in Scheme 30.[96]

The synthesis of D-homo-8-aza-17-oxasteroids was undertaken (Scheme 31)[97,98] by the method described in Scheme 11.

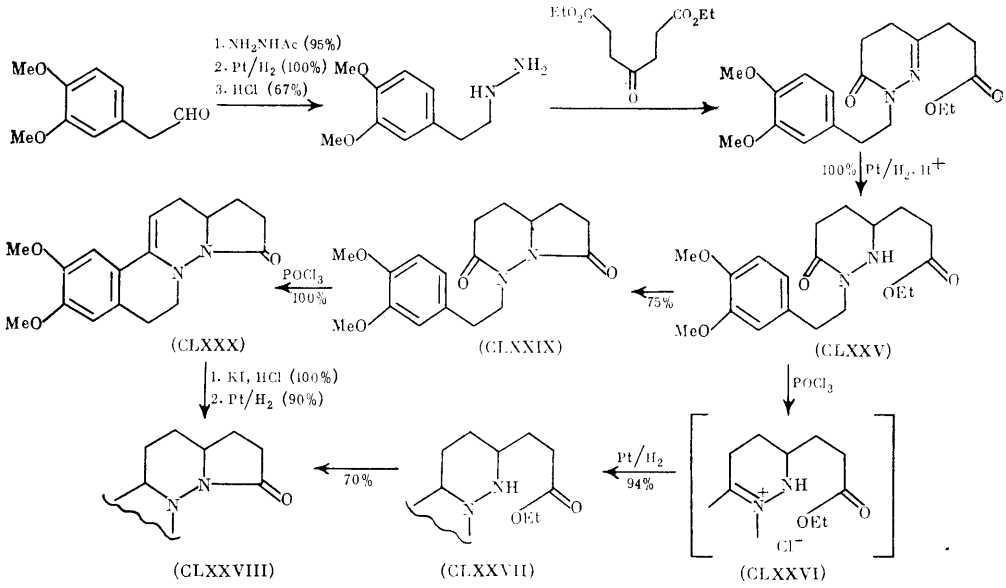
Scheme 25



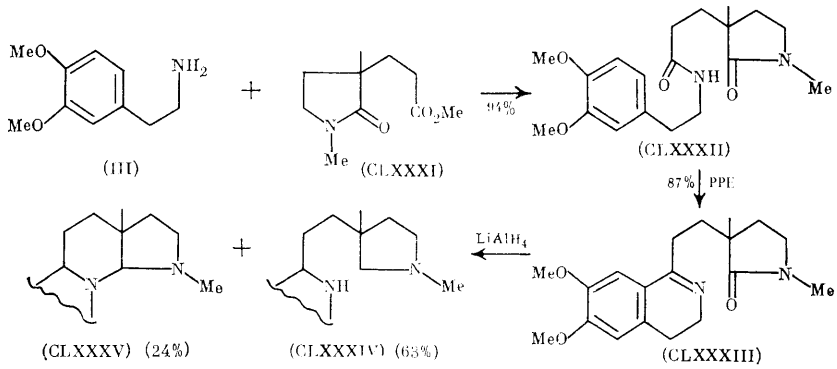
Scheme 26



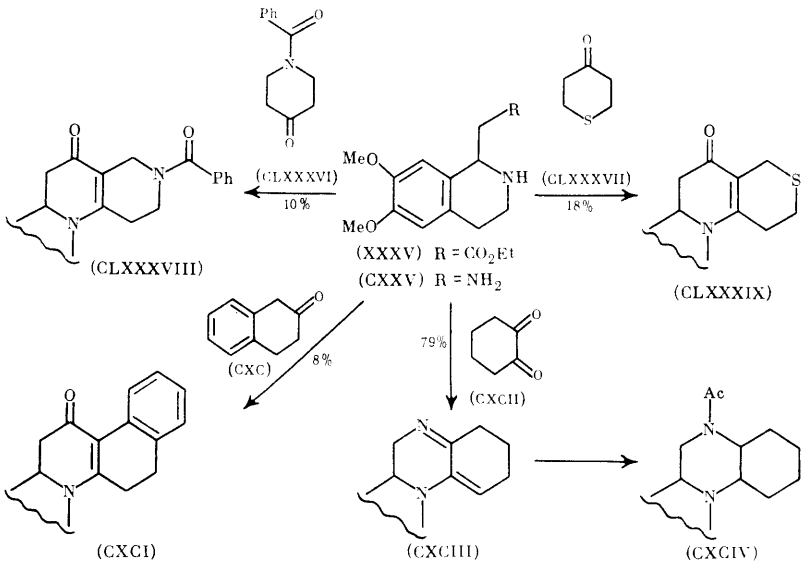
Scheme 27



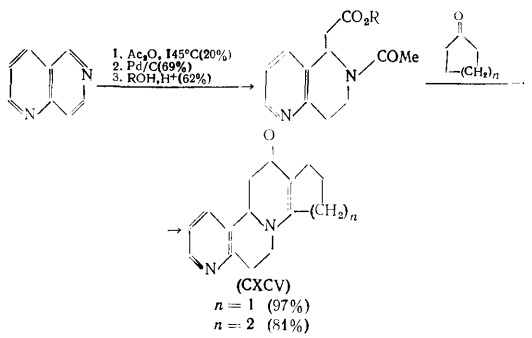
Scheme 28



Scheme 29



Scheme 30



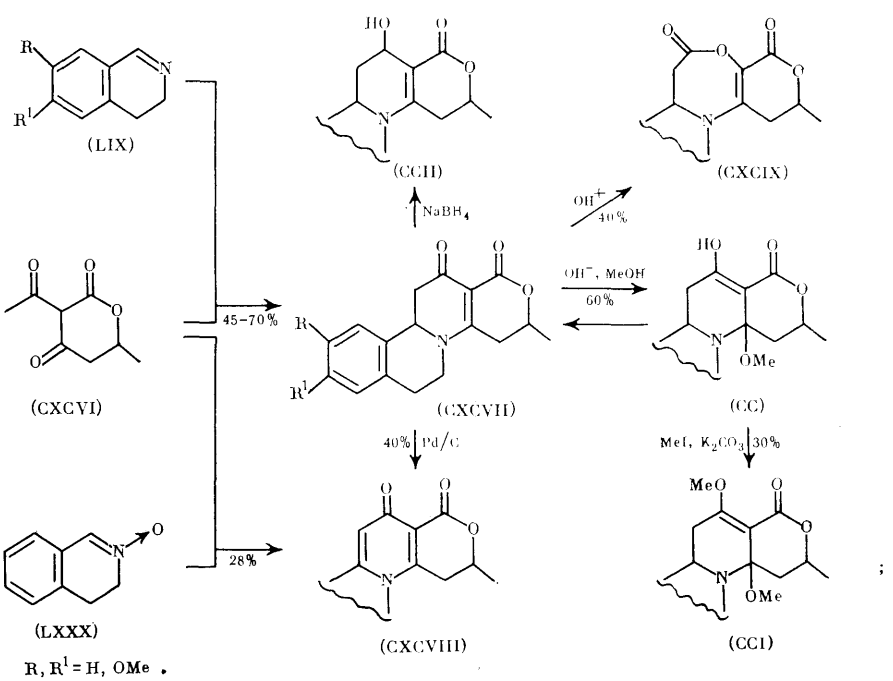
The use of the dihydrodehydroacetic acid derivative (CXCVI) in condensation with 3,4-dihydroisoquinolines (LIX) made it possible to obtain the tetracyclic enaminoketolactones (CXCVII). Like the enaminodiketones (LXIII), these compounds undergo dehydrogenation to form the γ-pyridones (CXCVIII) which are oxidised by monoperphthalic acid to the ε-lactones (CXCIX). Compounds (CXCVIII) have also been obtained by the condensation of 3,4-dihydroisoquinoline *N*-oxide (LXXX) with the acid (CXCVI).[48] The enaminoketolactones (CXCVII) showed a tendency to undergo certain reactions which are uncharacteristic of carbocyclic vinylogul lactams (LXIII). Thus, treatment with alkali in aqueous methanol gives rise to the aminoacetal (CC) whose content in the equilibrium mixture reaches 60%. Treatment of this mixture with methyl iodide in the presence of potassium carbonate in acetone produces the diester (CCI). Reduction of the enaminoketolactone (CXCVII) with tetrahydroborate gives rise to the hydroxypyrone (CCII).

When 3-acetyl-5-methyltetronic acid (CCIII) was condensed with the 3,4-dihydroisoquinolines (LIX), the enaminoketolactones (CCIV) of the 8-aza-16-oxasteroid series were obtained (Scheme 32).[99,100] These compounds are readily dehydrogenated to γ-pyridones (CCV) and give rise to the oximes (CCVI)[100] and thioketals (CCVII)[101] derived from the 12-oxo-group. Under the conditions of catalytic hydrogenation over the Adams catalyst, a mixture of three aminolactones (CCVIII), isomeric with respect to C(13) and C(15), was obtained[102,103] and their stereochemistry was established from infrared and ^{1}H NMR spectroscopic and mass-spectrometric data. Angular alkylation of the resulting aminolactones proceeds with total stereospecificity, producing two derivatives of 8-aza-16-oxaoestrone (CCIX) isomeric with respect to C(15) and having a *cis*-C/D-junction[102]. The 13- and 15-deutero-derivatives of compounds (CCVIII) and the 15-deutero-analogue of compound (CCIX) have been obtained and a mass-spectrometric study has been made of the dependence of the fragmentation and the peak ratios in the mass spectrum on the stereochemistry of the C/D-joined compounds (CCVIII) and (CCIX).[104]

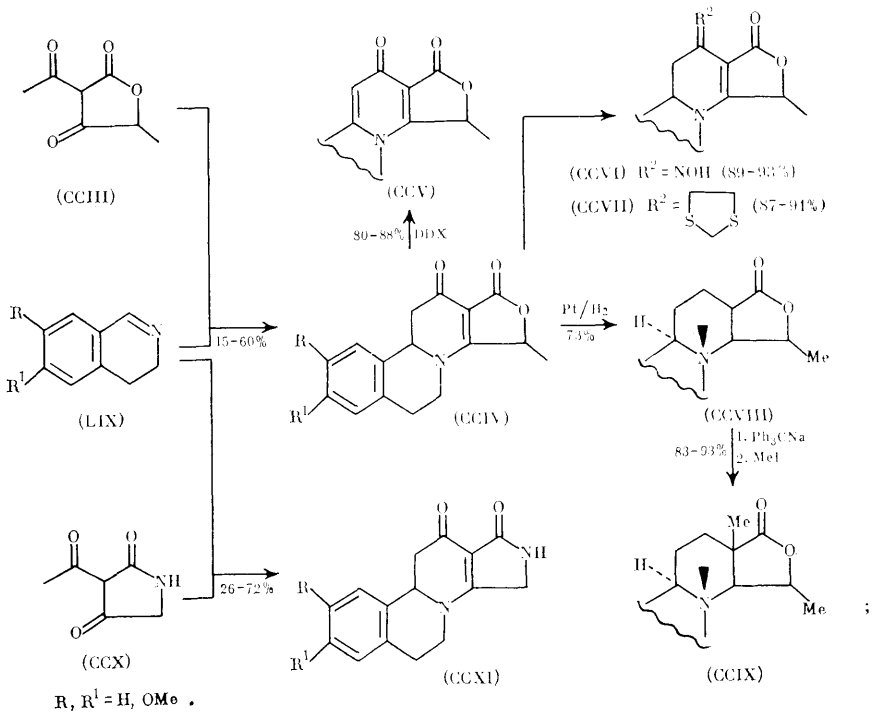
When 3-acetyltetramic acids (CCX) were condensed with the 3,4-dihydroisoquinolines (LIX), 8,16-diazasteroids (CCXI) were obtained (Scheme 32).[105]

6-Oxa-8-azasteroid (CCXVII) was synthesised in 1971 (Scheme 33).[106] For this purpose, the Mannich base obtained by the reaction of acetophenone (CCXII) with dimethylamine

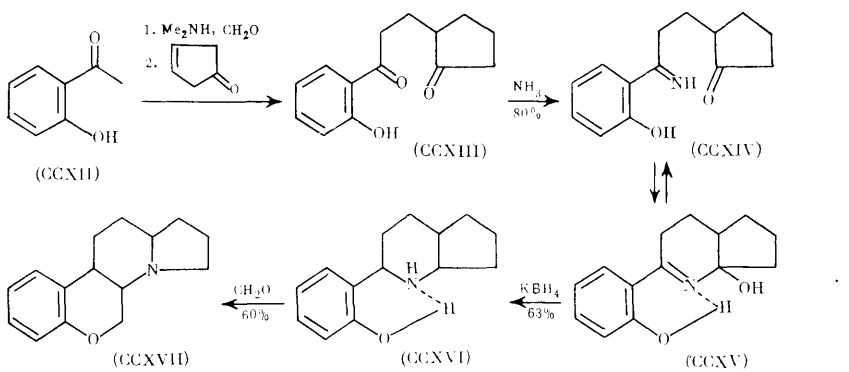
Scheme 31



Scheme 32



Scheme 33



and formaldehyde is condensed with cyclopent-3-enone. The resulting 1,5-diketone (CCXIII) gives rise to the iminoketone (CCXIV) on treatment with ammonia. The solid iminoketone exists in the cyclol form (CCXV). The reduction of the latter with tetrahydroborate results in the formation of the quasisteroid chelate (CCXVI), which gives rise to 6-oxa-8-azasteroid on treatment with formaldehyde.

V. BIOLOGICAL ACTIVITY OF 8-AZASTEROIDS

A common biological activity is not observed for different azasteroids, including 8-azasteroids and in this sense the term "azasteroid" indicates only that these heterocyclic compounds are structurally related. It has been observed that

many 8-azasteroids possess useful therapeutic properties characteristic of natural steroids or absent from the latter. Some 8-azasteroids showed a hormonal activity, but it is usually much lower than that of their carbocyclic analogues. Thus 8-azasteroids are a new class of biologically active compounds which are promising for the creation on their basis of new therapeutic preparations, exhibiting, in contrast to natural steroids, a selective action on the functions of the organism.

Thus compounds of type (XXIV) with an aromatic A ring[107], compounds (LIV),[108] compounds (VIII), compound (IX) and its 17-deoxy-derivatives, as well as their analogues containing double bonds in the 13-, 14-, and 16-positions[109,110] can be useful in the treatment of vascular collapse and serve as anti-shock agents. The hormonal activity of these compounds is insignificant. In particular the 3-methoxy-derivative (LIV, R=Me) exhibits 1/20 of the oestrogenic activity of mestranol,[29] while the oestrogenic activity of 8-azaquinoestrol (LIV), where the 3-methoxy-group has been replaced by the cyclopentoxy-group, does not exceed 1/20 of the oestrogenic activity of oestrone[111,112].

Semi-quantitative estimates of the anti-shock activities of a series of 17-deoxy-derivatives of 8-azasteroids (IX) and their quaternary salts of type (VIII) have been made and certain conclusions have been reached concerning the relation between the structure and activity[11]. Thus, in the case of free bases, phenols (containing OH groups in the 2- and 3-positions) proved to be less active than their methyl ethers, while the opposite relation has been observed for the quaternary salt. In the absence of the angular 13-methyl group, the activity of the methyl ethers of quaternary salts of type (VIII) remains unchanged but it diminishes in the phenolic quaternary salts and increases in the methyl ethers of the corresponding bases.

The 8-azasteroids (XVII) and (XVIII) as well as their analogues containing the 11-acetoxy-group and compound (XIX) can be useful in the treatment of vascular diseases and in endocrinology[113].

The 21-acyloxy-derivatives (XXXIII) exhibit a cardiotonic activity together with a weak hormonal activity[114]. The sulphur-containing 8-azasteroid (XXXII) and quaternary salts have analogous properties[115]. Compounds of types (XX) and (XXI) as well as their quaternary salts exhibit an anti-inflammatory activity in addition to the types of activity indicated above[116].

The sulphoxides of type (XXXI) and their 9(11)-dehydro-analogues possess cardiotonic and anti-fertility activities[117]. The 11-ketoximes of the 8-azasteroids (IX) can be used as anabolic preparations and the 17-amino-derivatives obtained from them are effective in the treatment of vascular collapse[118].

The oximes (XV) as well as their quaternary salts manifest cardiotonic and anti-inflammatory activities together with a hormonal activity, the extent of which has not been indicated[119].

The Δ^4-3-oxo-derivatives of the 8-azasteroids (X), (XI), and (XXIV) as well as their synthetic precursors, formed as a result of the Birch reduction of the aromatic ring, can be used as hypotensive preparations and in the treatment of vascular collapse and other cardiovascular diseases[120]. A hypotensive activity has been observed in the dienamines (LI).[121]

Compounds of type (XXIV) exhibit a gestogenic activity and in the case of compounds with the 13-methyl group this activity amounts to 1/40 of the gestogenic activity of progesterone, while the introduction of the 13-ethyl group increases this activity to 1/2–1.[13,30] A weak oestrogenic activity has been found in the 8-azaoestrone derivatives (IX) and (XLIX).[122]

Derivatives of 8-aza-19-nortestosterone (LIII)[123] and their synthetic precursors with a $\Delta^{5(10)}$-bond[124] exhibit gestogenic, androgenic, and anabolic activities. Thus the 17-ethynyl-13-methyl derivative (LIII) has 1/5 of the gestogenic activity of its carbocyclic analogue norethisterone. The introduction of the 13-ethyl group increases the gestogenic activity and approximately compensates for the decrease of this activity as a result of the introduction of the heteroatom. A weak antiandrogenic activity has been observed in the 17-ethyl derivative (LIII).[29]

The 12-oxo-derivatives of 8-azasteroids (XXXVIII) and their oximes (LXXV) exhibit a psychosedative activity[34]. They are also antidepressants and have been suggested as agents effective against Parkinson's disease[35].

Analgesic activity has been observed in the 8,13-diaza-steroids (CXXIV).[74,125]

The study of the biological activity of 8-azasteroid enaminodiketones of type (LXIII) showed that these compounds exhibit various types of pharmacological activity in the absence of hormonal activity[126]. Among compounds of this type, substances with anti-inflammatory, membrane-stabilising, and antifibrinolytic activities have been discovered[127–129]. Some of them manifest either immunostimulating or immunodepressing activities.

In the series of 8,16-diazasteroids of type (CCXI) and compounds based on them, substances have been found which stabilise the membranes of erythrocytes, the Erlich cells, and lysosomes and exhibit anti-inflammatory, anaphylactic, and cardiotonic activities[105,130].

Among 8-aza-16-oxasteroids of type (CCIV) and their derivatives and D-homo-analogues, compounds with anti-inflammatory, membrane-stabilising, and antifibrinolytic activities have been found[127,131].

During the preparation of the review for the press, new publications on the synthesis and properties of 8-azasteroids appeared. Thus a mass-spectrometric study has been made of the fragmentation and peak intensity ratios in the spectrum as a function of the stereochemistry of the B/C- and C/D-junctions in 12-oxo-derivatives of 8-azasteroids (XXXVIII) (Scheme 10).

The configuration of 12,16-dioxo-derivatives of D-homo-8-azasteroids (LXXXIII) has been studied by NMR (Scheme 11).[133] The signals corresponding to all the protons of the 8-azasteroid skeleton have been assigned and their spin–spin coupling constants have been found. The authors were unable to observe any kind of relation between the stereochemistry of the B/C-junction and the fragmentation in the mass-spectra of the compounds indicated. The deutero-analogues with respect to the C(11), C(15), and C(17) atoms were used.

An unsuccessful attempt at the synthesis of 8-aza-11-thia- and 8,13-diaza-11-thia-steroids has been described[134]. In the course of this investigation, compounds having the C-nor-D-homo-8-aza-11-thiasteroid skeleton were obtained.

A review of the syntheses and biological activities of 8-aza-, 8,16-diaza-, and 8-aza-16-oxa-steroids of types (LXIII) and (LXVII) (Scheme 11) and (CCIV) and (CCXI) (Scheme 32) was published in 1982.[135] The syntheses and biological activities of 8-aza-16-oxa- and D-homo-8-aza-17-oxasteroid enaminolactones, obtained from compounds (CXCVII) (Scheme 31) and (CCVII) (Scheme 32), have been described. It has been shown that these compounds exhibit anti-inflammatory, membrane-stabilising, and antifibrinolytic activities and, in terms of their effectiveness, they are superior to prednisolone without exhibiting a hormonal activity.

Anti-inflammatory, antiallergic, and immunotropic activities have been found in the series of 8-aza-, 8,16-diaza-, and

8-aza-16-oxa-steroids. Some of the data on their biological activity have already been published[141-146].

It has been shown[147] that 8-azasteroids interact with cytochrome P-450, certain kinetic parameters of the oxidation of these compounds by cytochrome P-450 have been investigated, and the characteristics obtained have been compared with the analogous characteristics of natural steroids.

A simple stereospecific synthesis of 8-aza-12-oxasteroids has been proposed[148].

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Institute of Bio-Organic Chemistry,
Academy of Sciences of the
Belorussian SSR, Minsk

Translated from *Uspekhi Khimii*, 53, 1045-1071 (1984) U.D.C. 547.963.4

The Oxidation of Haemoglobin

A.E.Myshkin

The literature data on the oxidation of human haemoglobin and the haemoglobin of other vertebrates in the form of complexes with ligands and in the free state are surveyed. The relation between conformational changes in oxyhaemoglobin and the rate of its autoxidation as well as the role of the chemical factors influencing the conformation of the protein, the active centre, and the rate of oxidation of haemoglobin are emphasised.
The bibliography includes 122 references.

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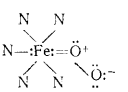
I. INTRODUCTION

Approximately 3% of the circulating haemoglobin (Hb) is oxidised daily in the blood of the adult human being[1]. The reductase systems in the erythrocyte reduce most of the oxidised haemoglobin. However, under these conditions, the blood contains permanently 1–2% of the oxidised form—methaemoglobin (Hb^+) relative to the total amount of the unoxidised and oxidised forms. The small amount of methaemoglobin in the blood plays a definite physiological role: in particular, methaemoglobin actively binds certain anions (CN^-, OCN^-, SCN^-, N_3^-, etc.) which have a high affinity for iron(III) and are capable of binding the iron in cytochromes and of blocking the respiratory chain of the mitochondria[2,3]. An increase of the concentration of methaemoglobin above 1–2% lowers the oxygen transport function of blood. This state, referred to in clinical practice as methaemoglobinemia, belongs to the class of dangerous pathological conditions and requires treatment when it is sufficiently acute. The causes of methaemoglobinemia can be various: hereditary breakdown of the primary globin structure, the breakdown of the functioning of the methaemoglobin reductase systems in the erythrocyte, and the entry into erythrocytes of methaemoglobin-forming substances of endogenic or exogenic origins. In all these cases, uselessly circulating methaemoglobin accumulates in the blood. The understanding of the mechanism of the oxidation of haemoglobin or more precisely of the oxidation of the haem iron of haemoglobin and the conditions promoting or hindering this process ultimately helps physicians to find ways of preventing or reducing methaemoglobinemia. The aim of the present review is to survey the existing literature concerning various pathways leading to the oxidation of haemoglobin with emphasis on the purely chemical aspects of this process.

In discussing the data, preference is given to human oxyhaemoglobin (if the origin of haemoglobin is not otherwise stipulated, human haemoglobin may be assumed). However, when interesting data of chemical importance are available, the haemoglobins of other vertebrate species are also considered. In a number of instances, deoxyhaemoglobin has been considered (in other words oxidation under anaerobic conditions) as well as other ligand derivatives of haemoglobin. The one-stranded haemoprotein myoglobin (Mb)—the oxygen-accumulating system in the muscle which has many properties in common with haemoglobin—is also considered in certain cases in the present review. Anomalous haemoglobins have not been dealt with because their wide variety and in many instances their unusual properties require their consideration in a special review. The fundamental ideas concerning the structure and functions of haemoglobin are also not described because such data have been frequently dealt with in various reviews, monographs, and textbooks. Sufficiently complete information about these questions in the Russian language can be found, in particular, in the review of Sharonov and Sharonova[4].

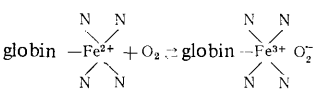
II. THE BOND BETWEEN THE HAEM IRON AND OXYGEN

Oxyhaemoglobin (HbO_2) is a diamagnetic complex of haemoglobin with molecular oxygen in which the haem iron formally retains the +2 oxidation state. The diamagnetism and geometry of this complex still constitute a topic which is attracting the attention of investigators. Among many of the models proposed, those of Pauling[5] and Weiss[6] have been most widely adopted. Pauling assumes that the bond between Fe(II) and O_2 is formed with participation of two *d* electrons of Fe(II) and two *p* electrons of the positively charged oxygen atom in the diamagnetic dipole $^+O-O^-$. The remaining four *d* electrons of the iron are located in its two t_{2g} orbitals, iron also being diamagnetic under these conditions. The structure of Pauling's complex can be represented as follows:



where N denotes the four pyrrole porphyrin atoms and one imidazole nitrogen atom of the histidine protein. The use of the isotope hybrid $^{16}O^{18}O$ in a complex with haemoglobin in the study of Raman spectra[17] has confirmed Pauling's model in which the Fe–O–O group forms an angle of 120°.

Weiss[6] assumes that, when the haem iron interacts with molecular oxygen, an electron is transferred from iron to oxygen:



The single unpaired electron of the iron atom in the $(Fe)^5_{1/2}$ state is then paired with the lone electron of the superoxide radical-anion $\dot{O}_2^-$ (henceforth designated simply by O_2^-) imparting diamagnetic properties to the complex. In support of his model, Weiss points out the known similarity

of the absorption spectra of HbO_2 and alkaline methaemoglobin HbOH. The structure of the complex of Hb with O_2 in which the charges are separated was subsequently supported by means of various methods[8-14]. It has been shown[15] that the length of the O–O bond and the frequency of its stretching vibrations in free O_2^- are the same as the analogous parameters of the O_2 ligand in HbO_2. The Raman spectra of HbO_2 and HbCO at 4 °C in the range 200 to 1700 cm^{-1}, obtained on excitation with a laser at a wavelength of 441.6 nm, agreed with the Raman spectra of the low-spin iron(III) complexes in Hb^+.[12] This justified the claim that the iron in HbCO, like that in HbO_2, is in the +3 oxidation state and is bound to the CO^- anion. However, within the framework of Pauling's model, a partial shift of electron density from iron to oxygen is also permissible. Calculations by various workers yielded different negative charges on oxygen: from 0.1 (Olafson and Goddard[16]) to −0.56 (Kirshner and Loew[17]). The calculated temperature dependence of the quadrupole splitting ΔE_Q in the Mössbauer spectrum of HbO_2 constitutes a satisfactory confirmation of Pauling's model[18]. The concept of the decisive role of the rotation of the O_2 bound to iron was used in the calculations. In the chosen model at a low temperature HbO_2 may exist in one of four potential wells of identical depth due to the interaction of the π^* orbitals of O_2 with the d_{xz} and d_{yz} orbitals of iron and the p_z orbitals of the four nitrogen atoms of the porphyrin. According to the calculation, the height of the barriers between the potential wells is 200 cm^{-1}. The calculated temperature variation of ΔE_Q, determined by the rotation of O_2, agrees exactly with the experimental value within the framework of Pauling's model.

An attractive model of the Fe–O_2 bond in HbO_2, having the electronic configuration of ozone, has also been proposed[19]. The formation of the O_2–O bond in ozone takes place without a marked influence on the O–O bond in the initial O_2 molecule. The singlet ground state of O_3 is stabilised by a three-centre four-electron π-bond. The deviation of the angle between the bonds in O–O–O from 90° (117°) can be explained mainly by the repulsion by the doubly occupied p orbitals of the extreme atoms. The following requirements must be met by Fe(II) for the formation of an analogous bond between the latter and O_2: (1) the presence of the d_z orbital with one electron for the formation of a σ-bond with the analogous p_z orbital of O_2; (2) the presence of the d_{xz} orbital with one electron for the formation of a bond with the π-electron system of O_2; (3) the absence of electrons from the d_{xy} orbital, since the latter is strongly antibonding in relation to the nitrogen atoms of the porphyrin (Fe–O_2 is located in the yz plane passing between the two nitrogen atoms of the porphyrin); (4) the location of the four remaining electrons in the $d_{x^2-y^2}$ and d_{yz} orbitals of iron. Finally the electronic configuration of iron in the proposed model of HbO_2 can be expressed as follows:

$$(d_{x^2-y^2})^2\,(d_{yz})^2\,(d_{xz})^1\,(d_{z^2})^1 \quad \text{or} \quad (t_{2g})^5\,(e_g)^1$$

Ab initio calculation for this model leads to a fully unpolarised Fe–O_2 system.

Thus the survey of the literature on the Fe–O_2 bond in HbO_2 leads to the conclusion that there exist sufficiently well-founded data in support of both ionic and covalent models. Since the main haemoglobin–oxygen dissociation process under normal conditions involves the elimination of the neutral O_2 molecule [Eqn.(1)], i.e.

$$HbO_2 \rightleftarrows Hb + O_2\,, \qquad (1)$$

$$HbO_2 \rightleftarrows Hb^+ + O_2^-\,, \qquad (2)$$

but at the same time there is always at least slight autoxidation of HbO_2 which can be formally described by Eqn.(2), it is reasonable to adopt the covalent bond between O_2 and Hb as the most probable, in conformity with Pauling's model or another similar model, where there is a partial transfer of electron density from iron to oxygen. In other words, it is logical to assume that under normal conditions the contribution of the $Fe^{3+}O_2^-$ structure to the bond between the haem iron and O_2 is fully realistic. However, the concept of a non-polar but effectively polarisable Fe–O bond, in which a negative charge is readily transferred to oxygen under conditions promoting the oxidation of the haem iron is also permissible.

It is likewise essential to note that, if there is an integral negative charge on the oxygen of HbO_2, this does not imply that the iron is in the +3 oxidation state, since the porphyrin system has a considerable capacity for compensating the electron deficiency at the central metal ion. It is difficult to infer the true oxidation state of iron in HbO_2 on the basis of all the available data. Therefore, designations such as Fe^{2+} and Fe^{3+} are in this instance extremely arbitrary and are more in the nature of descriptive symbols[20].

III. THE AUTOXIDATION OF OXYHAEMOGLOBIN

In conformity with the Eqn.(2) presented in the preceding Section, the simplest pathway leading to the oxidation of the haem iron is the dissociation of HbO_2 with the heterolytic rupture of the Fe–O bond. If the medium contains no oxidants other than oxygen molecules under these conditions, then such HbO_2 oxidation is referred to as autoxidation. The autoxidation can be facilitated by agents capable of interacting with O_2 and HbO_2 (reductants of all kinds) or of abstracting O_2^- (protons). Depending on the pH of the medium, the mechanism of the autoxidation of HbO_2 can vary significantly. It is therefore useful to consider this process separately in neutral, acid, and alkaline media.

1. The Autoxidation of HbO_2 in a Neutral Medium

It is known that HbO_2 is gradually modified on storage in neutral aqueous solutions and that one of the main characteristics of this process is the oxidation of HbO_2 to methaemoglobin. However, the low rate of oxidation of HbO_2 at temperatures $\leq$40 °C, where the thermal denaturation of the protein promoting the autoxidation does not play a significant role, hinders the systematic study of the autoxidation of HbO_2 in neutral media. It has been noted[20] that, in the autoxidation of HbO_2 in a neutral buffer, the maximum on the Soret band shifts from 412 to 405 nm, the intensity of the 541 and 575 nm band falls, and a band at 500 nm, characteristic of Hb^+, appears. It has been noted further that the oxidation of HbO_2 is accompanied by its degradation: the band at 280 nm is smoothed out. All these changes are accelerated in a more dilute HbO_2 solution (1.3×10^{-5} M) in which part of the HbO_2 is dissociated into dimers. It has been suggested[20] that the autoxidation of HbO_2 is accelerated by the hydrogen peroxide formed in the reaction, which has been confirmed by special experiments with added catalase, capable of decomposing H_2O_2, which inhibited the autoxidation of HbO_2.

The study of the kinetics of the autoxidation of HbO_2 in 0.1 M phosphate buffer at pH 7.2 showed that the reaction consists of two stages in which the rate constants for the individual stages are 0.032 h^{-1} (degree of reaction ~50%) and 0.0037 h^{-1}. Measurements were also made for the kinetics of the autoxidation of isolated chains under

analogous conditions at 25 °C. The rate constants for the autoxidation of the α- and β-chains proved to be 0.025 and 0.009 h^{-1}, which served as a basis for the assumption that the α- and β-subunits of HbO_2 are oxidised preferentially in the rapid and slow stages respectively. The latter was confirmed by the separation into the individual chains of ~30% oxidised HbO_2 after its treatment with CO and KCN: the isolated α-chains contained 53% of the cyanomet-form, while the β-chains contained only 5% of this form. The different tendencies of the α- and β-subunits of HbO_2 towards autoxidation enabled the authors to suggest that the transition $\alpha_2\beta_2 \rightarrow \alpha_2^+\beta_2^+$ proceeds via the intermediate semi-oxidised form $\alpha_2^+\beta_2$. The reduction of the partial pressure in the system from 57 to 40.5 mmHg increased the rate of autoxidation of mainly the β-chains.

The influence of the Cl^-, F^-, and N_3^- anions on the rate of autoxidation of HbO_2 has been studied at pH 7.4 and 37 °C.[22] The authors suggest that the mechanism of the autoxidation involves in this case the nucleophilic substitution of O_2^- by the corresponding anion. In contrast to the data of Shtamm et al.[20], single-stage oxidation kinetics were observed in this case. At a concentration of the anions of 0.1 M and an ionic strength of 0.5 (in the presence of added sulphate), the rate constants in the presence of Cl^-, F^-, and N_3^- were respectively 0.0229, 0.0348, and 0.175 litre $mole^{-1}$ h^{-1}. At the same time the E_{act} were found to be 32 kcal $mole^{-1}$ for the chloride anion and 26.8 kcal $mole^{-1}$ for the azide anion. Analogous studies by the same workers were carried out in the pH range from 5 to 9.3.[23] The activity sequence was established for a wider range of anions: $N_3^- > SCN^- > OCN^- > F^- > Cl^- > Br^-$. A mechanism was proposed in which the nucleophilic substitution by the superoxide anion by other anions is promoted by the attack of the proton on the oxygen bound to the iron. The low rate of the process compared with the rate of substitution at the haem iron of ligands such as N_3^-, OCN^-, and F^- is explained by the relatively low polarity of the Fe–O_2 bond and the necessity for additional energy to achieve its polarisation. The authors explained the decrease of the rate of autoxidation on passing from an acid to a neutral medium by the decrease of the concentration of the protons interacting with FeO_2.

The mechanism proposed[22,23] for the nucleophilic substitution of O_2^- by other anions is fairly convincing only for the azide anion, whose effect is greatly superior to those of the other anions. The virtual absence of this effect for HbCO (in this case nucleophilic substitution would have involved the unlikely elimination of CO^-) constitutes confirmation of this mechanism for the azide. The linear dependence of the pseudo-first order rate constant on the azide concentration is quoted as another piece of evidence. The absence of a similar linearity for the chloride anion throws doubt on the mechanism of the nucleophilic substitution of O_2^- by the chloride anion as well as other halide anions. According to the above data[22,23], the activity of the halide anions increases from bromide to fluoride in order of decreasing nucleophilicity of these anions in an aqueous medium (contrary to the authors' claim). However, the main objection is the possibility of non-specific and specific interactions of the anions with the protein, in particular in the region of the fixation of DPG, as a result of which the conformational equilibrium $R \rightleftharpoons T$ for HbO_2 is displaced to a greater or lesser extent towards the T-conformation, which can significantly increase the tendency of HbO_2 towards autoxidation. The influence of anions on HbO_2 has been discussed in detail[24].

Whereas the possibility of the nucleophilic substitution of the superoxide anion by salt anions as the sole pathway leading to the autoxidation of HbO_2 in the presence of salts is doubtful, the formation of O_2^- in the reaction medium in the autoxidation of HbO_2 has been quite reliably established. In particular, it has been observed that in the autoxidation of HbO_2 [25] the rate of reaction is inhibited to one-third by catalase. On the other hand, superoxide dismutase, which disproportionates O_2^-, inhibits the autoxidation only slightly. This has led to the conclusion that the O_2^- formed in the system is rapidly converted into H_2O_2, which is actively involved in the oxidation of HbO_2, ensuring its conversion into the oxidised form to the extent of one-third. An analogous effect has been observed also in the autoxidation of human HbO_2.[26]. In this case the reaction was carried out in 0.067 M phosphate buffer at pH 7.4 with added EDTA (to bind traces of Cu^{2+}) at 37 °C. A mechanism involving the following stages has been proposed:

$$\text{Fe (II) } O_2 \rightarrow \text{Fe (III)} + O_2^-,$$
$$\text{Fe (II) } O_2 + O_2^- + 2H^+ \rightarrow \text{Fe (III)} + O_2 + H_2O_2,$$
$$\underline{2\text{Fe (II) } O_2 + H_2O_2 + 2H^+ \rightarrow 2\text{Fe (III)} + 2O_2 + 2H_2O},$$
$$4\text{Fe (II) } O_2 + 4H^+ \rightarrow 4\text{Fe (III)} + 3O_2 + 2H_2O.$$

It follows from the above scheme that O_2^- participates actively in the autoxidation of HbO_2. This has been confirmed by the results of another study[27], whose authors suggest that O_2^- gives up one electron to the oxygen in HbO_2, after which the partially reduced oxygen [the superoxide anion bound to Fe(II)] abstracts a second electron from Fe(II) and binds two protons to form H_2O_2. In the native erythrocyte this process does not apparently play an appreciable role, since the concentration of superoxide dismutase in the native erythrocyte is ten times higher, according to the authors' estimate[27], than the concentrations sufficient for the complete suppression of the oxidative effect of O_2^-. The direct involvement of O_2^- in the oxidation of HbO_2 has also been confirmed for a system where O_2^- was generated by the oxidation of xanthine catalysed by xanthine oxidase[28]. The following reactions are postulated in this instance:

$$2H^+ + O_2^- + \text{Fe (II) } O_2 \rightarrow \text{Fe (III)} + H_2O_2 + O_2,$$
$$O_2^- + \text{Fe (III)} \rightarrow \text{Fe (II) } O_2,$$
$$2O_2^- + 2H^+ \rightarrow H_2O_2 + O_2.$$

It has been established that in a neutral medium the first of the above reactions is suppressed by the third after the attainment of an O_2^- concentration $>10^{-5}$ M. In a study with isolated chains[21] a higher rate of the autoxidation of the α-chains (0.025 h^{-1} at 25 °C) compared with the β-chains (0.009 h^{-1}) was observed. It was suggested that the valence hybrids $\alpha_2^+\beta_2$ are formed as intermediates in the autoxidation of HbO_2. This implies that, for example, in the observed 20% oxidation of HbO_2, 40% of the HbO_2 molecules are actually involved in the oxidation process. According to Tomoda et al.[29], in the autoxidation in 0.01 M phosphate buffer at pH 6.6–7.8 the rate constants for the formation of $\alpha_2^+\beta_2$ and $\alpha_2\beta_2^+$ are respectively 2.2×10^{-2} h^{-1} and 1.88×10^{-2} h^{-1}. The addition of inositol hexaphosphate (IHP) accelerated the oxidation of both subunits approximately by a factor of two in this instance.

The formation of valence hybrids in the autoxidation of haemoglobin can have serious physiological consequences. Analytic isoelectrofocussing in a polyacrylamide gel of the haemolysates of the blood of patients suffering from methaemoglobinemia with a more than 20% Hb^+ content revealed the presence of three fractions: HbO_2, Hb^+, and partly oxidised Hb.[30] The amount of the last fraction was 35–50% of the total amount of the haemoprotein. Thus the determination of the oxidised haemoglobin by the generally accepted Drabkin method yields the concentration of the oxidised haem, but not the amount of the haemoglobin tetramers involved in the oxidation. The increased affinity for oxygen and the almost total absence of cooperative

behaviour are characteristic of the valence hybrids (analogous data have also been obtained in another study[31]). The last two factors significantly impair the oxygen transporting capacity of the blood in patients suffering from methaemoglobinemia.

There are data[32] for the autoxidation of HbO_2 in the blood plasma at pH 7.5 and 37 °C. The results of the study of Mansouri and Winterhalter[21] have been confirmed: the decrease of the oxygen partial pressure in the blood plasma from 126 to 23 mmHg increased severalfold the rate of autoxidation of HbO_2.

The study using the HbO_2 from the frog *Rana esculenta*[33], chosen because of its high lability with respect to autoxidation, established that the rate of oxidation of this oxyhaemoglobin in 0.01 M phosphate buffer at pH 7.0 is significantly influenced by the heavy metal ions present in the buffer. The addition of EDTA greatly decreased the rate of autoxidation in this instance. In the absence of heavy metal ions, 7% of HbO_2 was found to be oxidised after 1 h at 2 °C and at an initial HbO_2 concentration of 1.5×10^{-5} M, whereas in the presence of added 10^{-4} M metals, the following amounts of oxidised HbO_2 were found: 28% for Cu, 16% for Zn, 5% for Sn, 11% for Fe, 14% for Cr, 18% for Mn, 16% for Hg, 11% for Pb, 17% for Co, 13% for Cd, and 20% for Ni. In particular, it was established that copper forms complexes with the imidazole groups of histidine and causes the denaturation of the protein, which is reversible in the presence of EDTA. The catalytic effect of heavy metals was also noted in the autoxidation of sperm whale or ox oxymyoglobin (MbO_2) in various buffers[34]. An equimolecular amount of Cu(II) accelerated in this case the oxidation by a factor of 25. The accelerating effect of Cu(II) on the autoxidation of the sperm whale MbO_2 at pH 5.0 [35] is explained by the binding of Cu(II) by the GH1 histidine, which interacts with haem and accelerates the delocalisation of the valence electron of the iron. According to the authors, this electron may fall into the potential well of the acceptor (the O_2 in the medium or Cu^{2+}) when the latter forms a complex in the region of His GH1.

It has been noted[36] that at pH 7 (0.05 M tris buffer) the addition of $ZnCl_2$, $PdCl_2$, and $CdCl_2$ did not entail spectroscopic changes in the HbO_2 solution, whereas the addition of $FeCl_2$, $FeCl_3$, $CuCl_2$, and $HgCl_2$ did lead to spectroscopic changes and the formation of a precipitate. It is remarkable that the presence of EDTA, which suppresses the effect of Cu(II), does not interfere with the oxidative activity of Fe(II) and Fe(III).

Apart from the study[35] quoted above, there exists a fairly extensive literature on the autoxidation of MbO_2. The exact determination of the amount of free O_2 evolved on formation of Mb^+ is important for the understanding of the mechanism of the autoxidation of MbO_2.[37] It has been shown that only 20% of the O_2 bound in MbO_2 (in the ox and sperm whale) is converted into water, while 75% is evolved in a free state. This suggested the following simple mechanism:

$$MbO_2 \rightleftarrows Mb + O_2 ,$$
$$Mb + H^+ + {}^1/_4 O_2 \rightarrow Mb^+ + {}^1/_2 H_2O .$$

This mechanism was confirmed by the dependence of the rate of autoxidation of MbO_2 on the O_2 concentration and the pH observed by the authors[37]: at pH 7 the autoxidation rate constants were found to be inversely proportional to $[O_2]$ and their logarithms increased linearly as the pH was reduced from 7 to 5. More detailed studies made it possible to elaborate further the above mechanism by including in the latter the intermediate O_2^- and H_2O_2 as oxidants[26]:

$$MbO_2 \rightarrow Mb^+ + O_2^- ,$$
$$MbO_2 + O_2^- + 2H^+ \rightarrow Mb^+ + O_2 + H_2O_2 ,$$
$$2MbO_2 + H_2O_2 + 2H^+ \rightarrow Mb^+ + 2O_2 + 2H_2O .$$

An unusual point of view concerning the possible mechanism of the autoxidation of HbO_2 has been put forward by Banerjee and Stetzkowski[38], who induced the autoxidation of HbO_2 by adding high-molecular-weight polypeptides obtained by the decomposition of horse heart Mb. In this case the transfer of haem from the haem pocket to the peptide was observed with formation of haemochrome. Peptides which readily bind ferrohaem, while the binding of ferrihaem is poor, are the most effective in the autoxidation of HbO_2. The following chain of transformations takes place in this case: the emergence of ferrohaem from the haem pocket, the binding of ferrohaem to the new ligand, the oxidation of ferrohaem, and the return of ferrihaem to the haem pocket. The process proceeds at the maximum rate when the haemoglobin is half-saturated by oxygen and is suppressed when its saturation is complete. Thus the autoxidation of HbO_2 in a neutral medium can be due to the oxidation of partly dissociated deoxyferrohaems derived from Hb in equilibrium with HbO_2. The initial ideas about the mechanism of the autoxidation of HbO_2 have been described in a monograph by Blyumenfel'd[39], who investigated the transfer of haem from haemoglobin to gelatin (the haem transfer reaction). However, in the absence of external ligands promoting the emergence of haem from the haem pocket, the haem dissociation mechanism of autoxidation gives rise to certain doubts bearing in mind that the α-subunits in HbO_2 are oxidised more readily than the β-subunits, while the bond between haem and the globin is stronger in the former than in the latter[21].

An approach to the understanding of the intimate mechanism of the autoxidation of HbO_2 in a neutral medium can be achieved by comparing this process with the autoxidation of protein-free iron(II) complexes. The principal possible mechanisms have been discussed in a review[40]. The simple bimolecular interaction

$$Fe(II) + O_2 \rightarrow Fe(III) + O_2^-$$

is an endothermic process and can hardly serve as a model of the main pathway in the autoxidation of HbO_2. The following scheme is more likely on energy grounds:

$$Fe(II) + O_2 \rightleftarrows Fe(II)O_2 ,$$
$$Fe(II)O_2 + Fe(II) \rightleftarrows Fe(II)O_2Fe(II) ,$$
$$Fe(II)O_2Fe(II) \rightarrow 2Fe(III) + O_2^{2-} \text{ etc.}$$

However, whereas this scheme is suitable for the porphyrin complexes of iron(II), in the presence of a protein environment the formation of a dimer is improbable. Finally, the process involving the transfer of an electron from the medium to the oxygen bound to iron(II) may play a definite role. This can be represented in the following scheme:

$$Fe(II)O_2 + H \rightarrow Fe(II)O_2H ,$$
$$Fe(II)O_2H \rightarrow Fe(III) + HOO^- .$$

However, this process too is relatively ineffective for HbO_2, since the O_2 in the haem pocket is protected from reductants by the distal histidine. There exists the view that the high oxidation-reduction potential of haemoglobin (+0.2 V at pH 7.0) is in fact largely due to this histidine[41].

2. The Autoxidation of HbO_2 in an Acid Medium

In a neutral HbO_2 solution there is a tetramer–dimer equilibrium [Eqn.(3)] which is largely displaced towards the tetrameric form of HbO_2 ($\alpha_2\beta_2$):

$$\alpha_2\beta_2 \rightleftarrows 2\alpha\beta \qquad (3)$$

A deviation of the pH of the solution from neutrality shifts the equilibrium towards the dimers. Even in a weakly acid medium (pH < 6) the concentration of the dimers is appreciable[42]. At pH < 4 considerable structural changes take place and are normalised by the prototropic groups masked in the protein. These include 18 of the 38 imidazole groups present in haemoglobin[43]. Dilatometric studies[42] have shown that at relatively high pH in the acid medium the volume of HbO_2 is somewhat increased, which is characteristic of globular proteins capable of being protonated. However, the protonation of HbO_2, starting from pH 4.5, results in a sharp decrease of the volume, which the authors explain by the intensified dissociation of HbO_2 into dimers.

The structural changes in carboxyhaemoglobin[45], whose conformation and properties are very close to those of HbO_2, have been investigated in detail in the pH range 3.3–1.8. It was noted that at pH > 3 the protein is uncoiled, while the haem remains bound to the native sections of the protein, although its environment is altered. At pH < 3, the structural changes in the protein are more significant: the uncoiling of the protein is accompanied by a considerable decrease of absorption in the region of the Soret band (there is a change in the character of the binding of haem) and also by the disappearance of the anomalous dispersion of the optical rotation and a change in absorption at 269 nm, both associated with the uncoiling of the protein globule. At pH < 2.1 almost all the haem is dissociated. In this case, the kinetics of the spectroscopic changes are independent of pH. It has been noted[46] that the absorption spectrum of the product of the denaturation of HbCO at pH 1.95 depends on the denaturation temperature (from 0° to 25 °C). The authors explain this by the splitting off of haem from the denatured product and its addition to another site in the protein, whose position depends on the process temperature. When the denaturation is carried out at pH 3.2, this type of temperature dependence of the process is not observed, which indicates the stability of the native bond between haem and globin at this pH.

The autoxidation of HbO_2 at a concentration of $\sim 3 \times 10^{-5}$ M has been investigated[47,48] in an acid medium at pH from 5.6 to 4.0 in the presence of various amounts of alkali metal salts. In all cases 0.1 M sodium acetate buffer solution was employed. The reaction rate constants, determined spectrophotometrically (at 576 nm), were mainly satisfactorily calculated in terms of a first-order process up to a considerable extent of reaction. The decrease of pH from 5.6 to 4.0 was accompanied by a linear increase of the logarithm of the rate constant. This justifies the attribution of the change in the activity of the protons of the medium in the above pH range to the same linearly varying factor. The observed linearity indicates a qualitative constancy of this factor as the activity of the proton is increased down to pH 4.0. This factor may be the conformational changes in the protein of HbO_2, which increases the lability of HbO_2 with respect to autoxidation. At the same time, these changes increase the degree of dissociation of HbO_2 into dimers and monomers. In the general case the dissociative-associative equilibrium for HbO_2 in various aqueous media is expressed by Eqn.(4), which supplements Eqn.(3), given above, by allowing for the possibility of the formation of monomers in the system:

$$\alpha_2\beta_2 \rightleftarrows 2\alpha\beta \rightleftarrows 2\alpha + 2\beta \,. \qquad (4)$$

Close to physiological conditions, reliable data concerning any kind of appreciable dissociation of haemoglobin into monomers are lacking, but monomers are detected when the deviation from neutral pH is considerable[49]. On the other hand, it is known that in a neutral medium chlorides increase the tendency of the monomeric subunits towards self-association[50,51] and the formation of the $\alpha\beta$ dimers[52]. Neglecting the possible difference between the rates of autoxidation of the α- and β-subunits, one can formulate a more general expression for the rate of oxidation of HbO_2:

$$\omega = -\frac{d[HbO_2]}{dt} = k_{obs}[HbO_2] = k_4[\alpha_2\beta_2] + k_2[\alpha\beta] + k_1[\alpha + \beta] \,, \qquad (5)$$

where k_4, k_2, and k_1 are the rate constants for the autoxidation of the tetramers, dimers, and monomers respectively and $[\alpha_2\beta_2]$, $[\alpha\beta]$, and $[\alpha + \beta]$ are the concentrations of the tetramers, dimers, and monomers respectively in terms of haem.

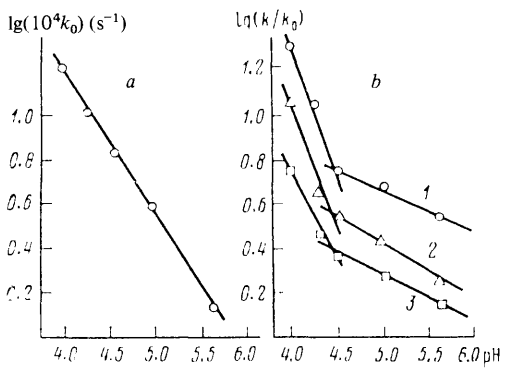


Figure 1. The pH dependence of the logarithm of the rate constant k_0 for the autoxidation of HbO_2 in the absence of chlorides (*a*) and the logarithms of the relative rates in the presence of KCl (*b*); $[HbO_2]_0 = 3 \times 10^{-5}$ M, 40 °C:[48] *1*) 0.333 M; *2*) 0.166 M; *3*) 0.083 M.

While the dependence of the rate of autoxidation of HbO_2 on the pH in the pH range 5.6–4.0 has no characteristic points[48], in the presence of alkali metal chlorides at concentrations up to 0.33 M, the pH dependen e of the logarithm of the rate constant has a sharp break at pH 4.5 (Fig.1). Presumably, there is a break in the curve for the pH dependence of the degree of tetramer–dimer dissociation at this pH in the presence of chlorides. The significant role of the chloride ion can be explained in this instance in the following manner. In the absence or at a low concentration of anions, the gradual increase of the activity of protons increases the number of protonated prototropic groups mainly in the imidazole and carboxylate residues. The accumulation of positive charges in the region of the α^1–β^2 contact increases the Coulombic repulsion of the dimers and gradually shifts the tetramer–dimer equilibrium to the right. In the presence of an electrolyte, the ionic strength of the medium at relatively high pH in the acid region intensifies the hydrophobic interactions between the dimers in the tetramers and to a certain extent prevents the dissociation of the latter (entropy factor). However, after the attainment of a certain level of protonation of the protein (tentatively in the region of pH 4.5), the region of the α^1–β^2 contact becomes readily accessible to the salt anions

as a result of the Coulombic repulsion of the dimers, the anions being directed to the positive charges on the protein mainly without loss of the hydration shell. Furthermore, as the protein is protonated its hydrophobic character diminishes. As a result of all these features, the role of the salt as a factor intensifying the hydrophobic interactions in the protein diminishes in a certain pH range, and the hydrated anions of the medium actually acquire the ability to enter the region of the contact between the $\alpha^1\beta^1$ dimers, destabilising the tetrameric structure. The simultaneous operation of these factors is apparently actually responsible for the appearance of a distinct break in the dependence of the rate of reaction on the pH in the presence of alkali metal chlorides. The dissociation of the $\alpha^1\beta^1$ dimers into monomers, which is possible at pH < 4.5 sharpens the break at pH 4.5. Speaking of the possible dissociation into monomers, the present author and Chundinova[47] emphasised that it is not obligatory to assume the formation of monomers separated by the medium when the "dissociative" influence of the pH on the autoxidation of HbO_2 is discussed: the cause of the strong effects on the autoxidation of HbO_2 can be also the weakening of the $\alpha^1-\beta^1$ contact as a consequence of the conformational changes in the monomers forming part of the dimers, preceding and determining the dissociation of the latter into monomers.

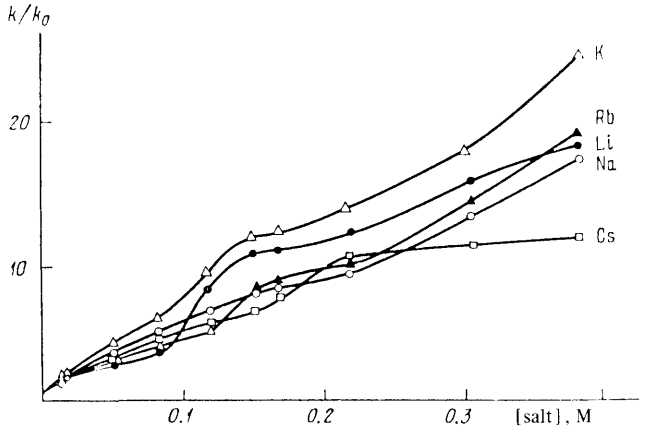


Figure 2. Dependence of the rate of autoxidation of HbO_2 on the concentration of alkali metal chlorides at pH 4.0 and 40 °C; $[HbO_2]_0 \cong 3 \times 10^{-5}$ M (in terms of haem).[47]

It has been established[47,48] that salt cations in an acid medium exert a very distinct influence on the rate of autoxidation of HbO_2. Fig.2 illustrates the curves for the dependence of k/k_0 (where k_0 is the rate constant in the absence of added salt) on the salt concentration for alkali metal chlorides at pH 4.0. The potassium cation is the most active and the caesium cation is the least active at concentrations above 0.25 M. At pH 5.6 the difference between the effects of the individual cations is more appreciable and in this case caesium is also the most passive. At pH 4.0 differences were also demonstrated between the effects of a series of anions. Fig.3 shows that the anions form the following sequence in terms of their accelerating effect on the autoxidation of HbO_2: $F^- < Cl^- < Br^- < I^- < ClO_4^-$.

This sequence is almost identical with Hofmeister's classical lyotropic series. The arrangement of the anions in conformity with the lyotropic series had been observed earlier for the dissociation of HbCO into dimers in a neutral medium under the influence of different sodium and potassium salts[54]. The closeness of the dissociation series to the series of anions in terms of their accelerating effect on the autoxidation of HbO_2 confirms the hypothesis[47,48] that there is a definite similarity between the mechanisms of the processes leading to the dissociation of HbO_2 into dimers and monomers and to its autoxidation.

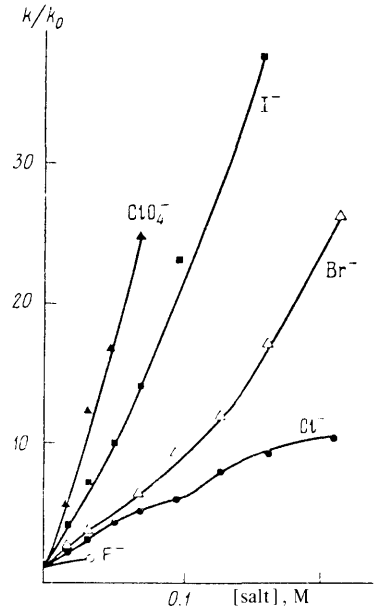


Figure 3. The influence of the sodium salt concentrations on the autoxidation of HbO_2 at pH 4.0 and 40 °C; $[HbO_2]_0 \cong 3 \times 10^{-5}$ M, $k_0 = (11.9-15.6) \times 10^{-4}$ s^{-1}.[47]

The influence of the nature and concentration of a series of carboxylate buffer anions on the autoxidation of HbO_2 has been investigated[55]. It has been observed that at pH 5.6, where HbO_2 is mainly tetrameric, and at pH 4.0, where HbO_2 exists preferentially in the form of dimers, the character of the influence of different carboxylate ions is significantly different. Fig.4 presents a plot of the logarithms of the rate constants for the autoxidation of HbO_2 at 40 °C against the molarity of the buffer. At pH 5.6 carboxylates can be clearly divided into three groups: alkanoates, chloroacetate (in the presence of which the reaction is 4–8 times slower than in the presence of alkanoates), and citrate, which gives rise to a complex concentration dependence. It is seen that small amounts of added alkanoates (up to ~0.2 M) have the most appreciable effect on the autoxidation of HbO_2. The chain length of the alkanoic acid has almost no influence on the effect under these conditions. At pH 4.0 the picture is different. If account is taken of the degree of dissociation of the alkanoic acids at this pH, then the alkanoates give rise to an almost linear dependence of the logarithm of the rate constant in the sequence formate < acetate <

propionate < butyrate, the rate in the presence of the butyrate, when the molarity of the buffers is 0.2 M, exceeding approximately by a factor of 15 the rate in the presence of the acetate. Hence it follows that, under conditions where HbO_2 is almost fully dissociated into dimers, non-polar agents modify extremely effectively the structure of HbO_2, rendering it significantly less resistant to autoxidation, which is not observed for the tetrameric structure of HbO_2 (pH 5.6). Consequently, the tetrameric HbO_2, whose outer surface is mainly hydrophilic, is relatively insensitive to non-polar agents, while the dimeric HbO_2, which has an open $\alpha^1-\beta^2$ contact surface with large hydrophobic sections, is extremely sensitive to non-polar agents.

Parameters of the Arrhenius equation for the oxidation of the sperm whale MbO_2 in 0.015 M tris–phosphate buffer[57].

pH	$t = 10-20°$			$t = 25-35°$		
	$\Delta G^{\neq}_{20}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$, e.u.	$\Delta G^{\neq}_{29}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$, e.u.
5.0	3.59	6.4	9.6	3.48	20.8	59.1
5.4	3.72	6.8	10.5	3.63	22.0	62.7
5.8	3.66	9.2	18.9	4.05	26.0	74.9
6.0	3.98	11.6	26.0	4.20	29.6	86.7
6.4	4.49	19.2	50.2	4.65	37.2	111.1
6.8	5.33	28.8	80.1	5.06	44.0	132.9

Measurements have been made for the kinetics of the denaturation of horse HbO_2 in the pH range 3.6–2.4 at 0 °C.[56] With decrease of pH in the above range, the first-order rate constant increased exponentially. Comparing this finding with the data of the present author and Chudinova[48], one can assume that, in the absence of an excess of salts, the denaturation and autoxidation processes (stimulated in all probability by the same factors), involving HbO_2 from different species, are proportional to the activity of the protons over a fairly wide pH range in the acid region.

Data on the autoxidation of ox MbO_2 at pH 7.0–5.0 [37] provide some justification for extending this pH range to 7.0. At the same time, it must be emphasised yet again that the "dissociative" mechanism of the autoxidation of HbO_2 formulated above presupposes conformational changes in the protein preceding the dissociation of the haemoglobin into subunits and not the dissociation itself. The character of these changes is apparently mainly the same as for the one-stranded myoglobin, which is confirmed by the linear dependence of the rate constant for the autoxidation of MbO_2 on the activity of protons[37].

The main parameters for the oxidation of the sperm whale MbO_2 have been determined in the pH range 7–5 in 0.015 M tris–phosphate buffer[57]. A linear dependence of the quantity $\lg [V/(1 - V)]$, where V is the Mb^+ concentration at a specific instant during the initial period of the reaction, on the pH was observed at 35 °C. Bearing in mind that the slope of this relation is two, the authors suggested that the autoxidation of MbO_2 is catalysed by the protonation of two histidine residues. The curve for the temperature variation of the rate of reaction has a break between 20° and 25 °C. The parameters of the Arrhenius equation observed at different pH are listed in the Table. The difference between these parameters for the temperature ranges 10–20° and 25–35 °C provided the authors with the grounds for the claim that there are two mechanisms of the autoxidation of MbO_2. It has been observed that the dependence of $\ln k$ on $\sqrt{I}$ (I is the ionic strength of the solution) at different temperatures is a minimum at $\sqrt{I} \cong 0.2$. The decrease of the rate of autoxidation of MbO_2 with increase of the ionic strength of the solution up to $I = 0.04$ is explained by the authors by the shielding of the positively charged groups of the protein, which are important for the autoxidation of MbO_2.

In conclusion of this Section, one can briefly formulate the principal possible causes of the acceleration of the autoxidation of HbO_2 in acid media. These may be (1) the conformational changes induced by the protonation of the weakly basic centres of the protein accompanied by the tetramer–dimer and dimer–monomer dissociation; (2) the protonation of the distal histidine, which enhances the hydrophilic properties of the haem cavitity, which can

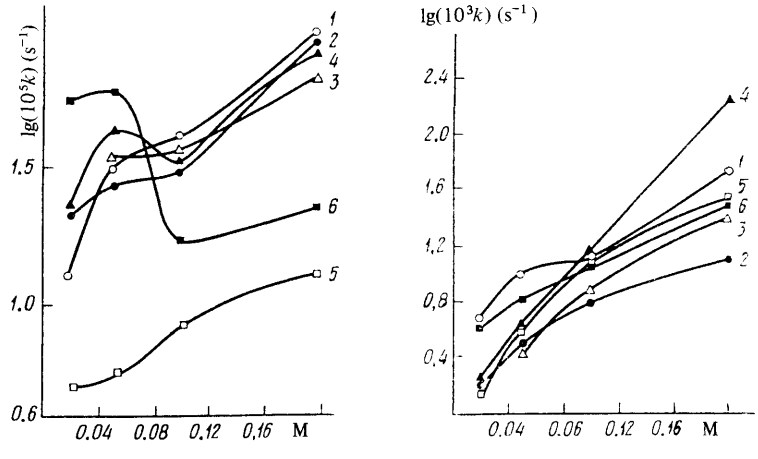


Figure 4. Dependence of $\lg k$ for the autoxidation of HbO_2 on the molarity of the buffer systems at 40 °C and $[HbO_2]_0 \cong 3 \times 10^{-5}$ M: *a*) pH 5.6; *b*) pH 4.0; *1*) formate buffer; *2*) acetate buffer; *3*) propionate buffer; *4*) butyrate buffer; *5*) chloroacetate buffer; *6*) citrate buffer[55].

facilitate the approach of the anions from the external medium to the iron and the emergence of O_2^-; (3) the protonation of the O_2 bound to the iron which promotes the electron transfer from Fe(II) to O_2 with subsequent elimination of HOO$^{\cdot}$.

3. The Autoxidation of HbO_2 (and the Oxidation of HbCO)

The mechanism of the action of alkali on haemoglobin has been most fully investigated by Perutz[58]. The main ideas reduce to the following. The free energy of the spherical polyelectrolyte is proportional to the square of its purely surface charge, as a consequence of which the stability of the polyelectrolyte diminishes on either side of the isoelectric point during the discharge of the cationic or anionic groups. Titration with acid or alkali can ionise the weak acids or bases concealed in the non-polar nucleus. After ionisation, these groups attract the hydration shell, which alters the native structure of the protein and shifts the equilibrium towards the uncoiled form. Three haemoglobins have been compared: human haemoglobin A, foetal haemoglobin (F), and ox haemoglobin. In 0.1 M NaOH at 20 °C, HbCO(A) is denatured in 20 s and HbCO(F) is denatured after 12 min, while the denaturation of the ox HbCO in 0.5 M NaOH has a 3 h half-decomposition period. Furthermore, it is known that all three haemoglobins dissociate into dimers at pH > 10. Hence follows the conclusion that the dissociation into dimers is reversible and does not constitute denaturation in the strict sense of the term. After the attainment of pH 11.6, the HbCO(A) dimers are cleaved and denatured, while the dimers of the two remaining HbCO are denatured only under more severe conditions. It has been suggested that this stage is in fact rate-limiting. Detailed analysis of the aminoacid composition of the three haemoglobins and comparison of the pK_a of various aminoacid residues led Perutz to the following conclusion: the cause of the instability of HbA in alkali is the presence in the latter in the region of the $\alpha^1-\beta^1$ contact of two Cys (G11α and G14β) units and also of Tyr H8β. In water the pK_a of the sulphhydryl groups of cysteine is 9.1–9.5 and that of the tyrosine hydroxyl is 9.5–10.0. Since these groups are strongly masked in haemoglobin, their true pK_a's are higher, but all these groups are undoubtedly ionised at pH > 12. Foetal haemoglobin has only one of the three residues specified (Cys in the γ-chain), while ox haemoglobin contain no such groups at all, which is the cause of its extremely high stability in alkali. Fig.5 illustrates schematically the dissociation of the dimer and the uncoiling of the monomeric chains under the influence of alkali. The author notes in this connection that there is no reliable information showing whether the dissociation into monomers or denaturation is the primary process.

The influence of the pH of the solution on the rate of autoxidation of human HbO_2 in the NaOH–glycine buffer in the pH range 9.0–12.0 at 40 °C has been studied in detail[59]. The observed relation is illustrated in Fig.6, which shows that the rate of autoxidation, which increases monotonically with increase of pH over the entire range investigated, gives rise to a pH dependence consisting of four clearly distinct sections. In the pH range 9–10 the rate constant increases linearly from 0.75 to 1.6×10^{-5} s^{-1}, i.e. approximately by a factor of 2. According to the available data for HbCO,[60] the concentration of the dimers increases approximately by a factor of 2 in the same pH range—from ~12 to ~24%. This agreement suggests that the rate of autoxidation of HbO_2 in the pH range 9–10 is determined mainly by the degree of tetramer–dimer dissociation. In the pH range 10–10.6 the rate constant increases linearly almost by an order of magnitude. Presumably the sharp break in the relation at pH 10.0 is caused not only by the rapid increase of the concentration of dimers (approximately by a factor of 3) but also by the conformational changes in the dimers formed. Next, the curve for the relation exhibits a further two breaks: at pH 10.6 and 11.6. The temperature variations of the rate of autoxidation have been determined for all three pH values and the following activation parameters have been calculated:

pH 10.7 $E_{act} = 60.3$ kcal mol^{-1}, $\Delta S^{\neq} = +116$ e.u., $\Delta G^{\neq} = 25.2$ kcal mol^{-1};
pH 11.45 $E_{act} = 18.7$ kcal mol^{-1}, $\Delta S^{\neq} = +15.7$ e.u., $\Delta G^{\neq} = 21.4$ kcal mol^{-1};
pH 12.0 $E_{act} = 10.9$ kcal mol^{-1}, $\Delta S^{\neq} = -36.7$ e.u., $\Delta G^{\neq} = 19.9$ kcal mol^{-1}.

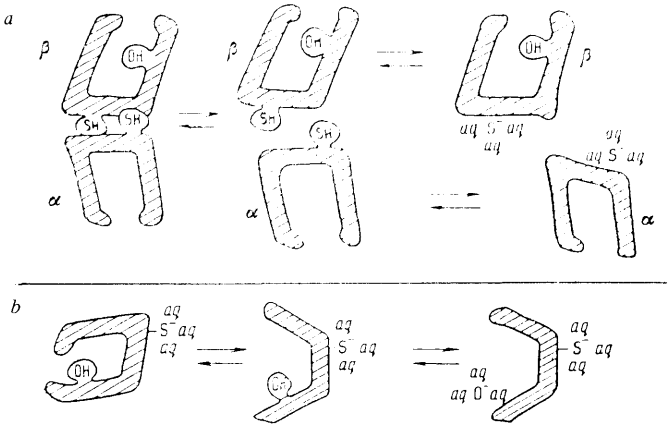


Figure 5. Schematic representation of the alkaline denaturation of haemoglobin according to Perutz[58]: *a*) dissociation of the dimer and ionisation of cysteine; *b*) uncoiling of the monomer and ionisation of tyrosine.

High enthalpies and entropies of activation are characteristic of the denaturation of proteins, in particular at pH 8, $E_{act} = 77.3$ kcal mol^{-1} and $\Delta S^{\neq} = 153$ e.u. for the thermal denaturation of human HbA.[61] On the other hand, the activation energy for the transition Fe(II) → Fe(III), involving simple iron complexes in the reaction with O_2, is of the order of 12–15 kcal mol^{-1}.[62,63] A negative entropy of activation for the oxidation reaction is also characteristic of all simple complexes. All these factors suggest that at relatively low pH values (9–10.5) the rate of autoxidation of HbO_2 is limited by conformational changes in the protein; on the other hand, with increase of pH their rate increases and the rate-limiting stage becomes the oxidation of iron in the already denatured haemoglobin (possibly in the dissociated haem). An attempt has been made at the interpretation of the kinetic results by comparing them with the absorption spectra in the range 245–320 nm at 10 °C (in order to detect only rapid conformational changes in HbO_2 under the influence of alkali). As was to be expected, an increase of pH from 9 to 10 hardly affects the spectrum. At pH 11, there is an appreciable increase of the absorption in the range 250–260 nm (normalisation of phenylalanine) and a shoulder appears in the range 285–295 nm (tryptophan, tyrosine). At pH 12 and 13 the spectral changes become more distinct. Thus one can assume that at pH 11 appreciable conformational

changes in HbO_2 already occur and these can cause, in particular, the unmasking of the tyrosine and the unreactive cysteine residues, whose ionisation, in conformity with the ideas of Perutz[58] and the present author and his co-workers,[59] leads to accelerated denaturation and autoxidation of HbO_2.

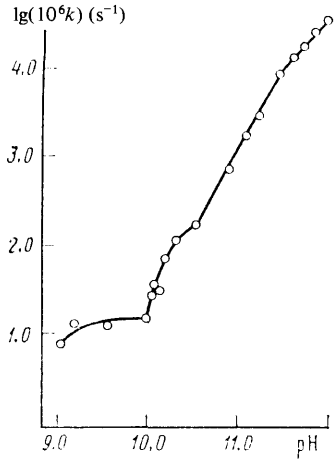


Figure 6. Dependence of $\lg k$ on the pH in the alkaline region for the autoxidation of HbO_2 at 40 °C; $[HbO_2]_0 \cong 3 \times 10^{-5}$ M.[59]

The kinetics of the oxidation of HbCO at pH 11.0–11.9 at 39 °C have been investigated[64] in the absence of molecular oxygen. In contrast to the data obtained in the study by Wallace et al.[23], where HbCO was oxidised at neutral pH in the presence of azide anions more slowly by 6–8 orders of magnitude than HbO_2, the rate of oxidation of HbCO in an alkaline medium proved to be comparable to the rate of autoxidation of HbO_2. Furthermore, the break observed in the dependence of $\lg k$ on pH for HbO_2 [59] was reproduced also for HbCO, although at a somewhat lower pH (11.4). This permitted the conclusion that, in the pH range 11–12, the mechanism of the oxidation of HbO_2 is the same as that of the oxidation of HbCO. In all probability at pH ranging from 11 to 11.4–11.6 the rate of oxidation of both HbO_2 and HbCO is limited by the protein denaturation stage, while at higher pH the rate-limiting stage is the oxidation of the denatured haemoprotein. The activation energy for the oxidation of HbCO at pH 11.65 (15.3 kcal mol^{-1}) is virtually identical with the corresponding value for HbO_2. At pH close to 12 the rate constants for HbO_2 and HbCO are very similar, whence follows the conclusion that in both cases the rate-limiting stage at high pH involves the transformation of the same substrate. Presumably the substrate is deoxyferrohaem. The nature of the direct oxidant of iron in HbCO was not elucidated in the present author's study[64]. Oxidation under aerobic conditions hardly altered the rate constant. In contrast to the first-order oxidation of HbO_2 which proceeds smoothly, the oxidation of HbCO takes place as a two-stage process—the first, faster stage continues up to ~50% degree of reaction.

The autoxidation of HbO_2 has been investigated in the presence of 0.01 M KCN without a buffer (pH ~10.4) with the addition of various amounts of primary normal aliphatic C_1–C_8 alcohols[65]. The comparative catalytic activity of the alcohols varies in this sequence as follows: 1; 2.2; 7.2; 17.5; 47.1; 893; 4010; 7500. The sharp increase of the activity of the alcohol on passing from 1-pentanol to 1-hexanol is noteworthy. This is probably associated with the greater capacity of 1-hexanol and higher-molecular-weight alcohols with a straight chain for insertion via the chain into the internal and mainly hydrophobic regions of haemoglobin.

The greater importance of non-polar effects compared with polar effects was manifested even more distinctly in the oxidation of HbCO in an alkaline buffer (pH 11.35) in the presence of tetra-alkylammonium bromides[66]. Tetramethylammonium bromide at concentrations up to 0.04 M (HbCO concentration 3×10^{-5} M) hardly influenced the rate of oxidation of HbCO. Its tetraethyl homologue showed a significant accelerating effect, while 0.01 M tetrabutylammonium bromide approximately doubled the rate of oxidation of HbCO.

Measurements have been made of the rate of autoxidation of HbO_2 in an alkaline medium in the presence of several stable nitroxy-radicals of the piperidine series[67]. The kinetic data made it possible to estimate the ability of these compounds to interact with HbO_2. The acceleration of the autoxidation of HbO_2 was determined as a measure of the conformational changes in the globin in the presence of different amounts of stable radicals up to the molar ratio radical : haem = 10 : 1. At pH 10.75 it was established that the 2,2,6,6-tetramethylpiperidin-1-yloxy-radical and its 4-oxo and 4-hydroxy-derivatives, which are widely used in the spin probe method, increase the rate of autoxidation of HbO_2 by a factor of 1.5–2 at the maximum concentrations employed. A somewhat greater effect (acceleration by a factor of three) is shown by the 2,2,6,6-tetramethyl-4,4-dinitropiperidin-1-yloxy-radical, which had not been used earlier in practice. Its 4-chloro-4-nitro-analogue proved to be still more active (acceleration by a factor of five). The geminal chloro- and nitro-groups apparently enable this nitroxy-radical to be bound specifically to particular polar centres of the HbO_2 molecule. At lower pH the influence of the nitroxy-radicals on the kinetics of the autoxidation of HbO_2 is less pronounced.

4. The Influence of Sulphydryl Reagents on the Autoxidation of HbO_2 (and the Oxidation of HbCO)

It is known that the blocking of the sulphydryl groups of haemoglobin by organomercury compounds, in particular by *p*-chloromercury benzoate (PCMB) promotes the dissociation of haemoglobin into dimers and monomers, which can be used to prepare isolated haemoglobin subunits[68]. It has been established that in the presence of an excess of PCMB the degree of dissociation of human haemoglobin into subunits depends on the concentration of the added NaCl, the degree of dissociation being a maximum in the presence of 0.1–0.2 M NaCl.[69] At a constant NaCl concentration (0.2 M) in the pH range 5.5–7.5 the degree of dissociation increases with decrease of pH and becomes complete already at pH 6 (at lower pH a precipitate is deposited). At pH 9–11, the dissociation of HbCO is incomplete and its extent decreases with increase of pH. Electrophoretic analysis showed that at low PCMB concentrations isolated subunits do not appear. Small amounts of the subunits are present when the PCMB : Hb ratio is 4 : 1 and a complete separation into subunits is achieved with the ratio 6 : 1. On the basis of these data and comparative data on foetal haemoglobin, the following conclusions have been reached: the reaction of PCMB with reactive SH groups (β-93) leads to the dissociation of HbCO into dimers; the reaction with β-112 SH-groups begins before the completion of the dissociation into dimers

and competes with the reaction of PCMB with the β-93 SH-groups. The dissociation into dimers is completed after both β-SH groups have reacted. The α-104 SH groups react with PCMB only after the completion of the reaction of the latter with the β-112 SH groups. The latter limitation is not obligatory at low pH, for example, at pH 4.7.

It has been noted[70] that, although the β-93 SH groups are not involved directly in cooperative interactions, the position of these groups in the mechanically important region of the protein makes their modification important for the state and functioning of HbO_2. Directly next to the β-93 SH groups on the surface of the $\alpha^1-\beta^2$ contact, there is histidine β-92 (the proximal histidine) and aspartyl β-94—the residue stabilising the deoxy-conformation of the C-end and of the β-chain as a result of the formation of a salt bridge with the His β-146 side chain. This interaction is directly associated with the Bohr effect and involves a cooperative mechanism. There are data showing[71] that the modification of the β-93 SH groups by a number of phenylmercury chloride derivatives increases the affinity of Hb for O_2. An analogous conclusion has been reached also for haemoglobin modified by cystamine and the dimethyl ester of cystine in acid and neutral media[72]. The Bohr effect then diminished and the shape of the oxygen equilibrium curves remained almost unaltered.

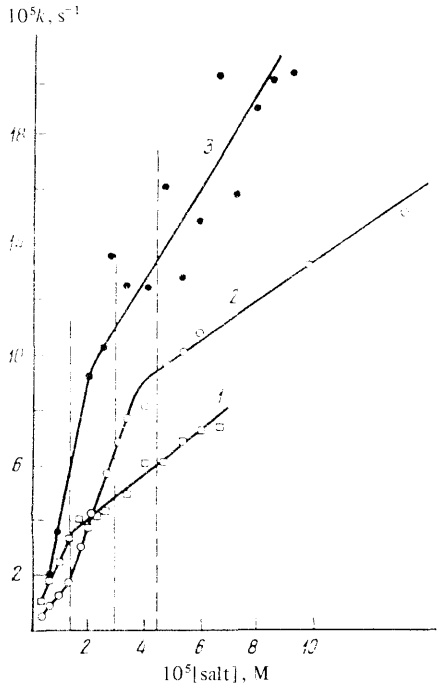


Figure 7. Dependence of the rate constant for the oxidation of HbCO in acetate buffer at pH 4.0, 30 °C, and $[HbCO]_0 = 3 \times 10^{-5}$ M on the concentrations of phenylmercury acetate (curve *1*), benzylmercury acetate (curve *2*), and mercury acetate (curve *3*).[74]

It has been observed[73] that the absorption spectra of Hb at pH 5.5–5.8 with added mercury(II) chloride resemble the spectra in the early stage of the acid denaturation of Hb (at pH 3, the Soret peak is reversely displaced to the region 370–390 nm and suffers an appreciable loss of intensity). Hence follows the conclusion that $HgCl_2$ interacts both with SH groups and with the imidazole residues of the protein.

The rates of oxidation of HbCO at pH 4.0 in the presence of phenylmercury acetate, benzylmercury acetate, methoxycarbonylmercury chloride, and mercury acetate have been measured spectrophotometrically at 30 °C and at a wavelength of 574 nm.[74] Fig.7 presents the curves for the dependence of the rate constant for the oxidation of HbCO on the concentrations of phenylmercury acetate, benzylmercury acetate, and mercury acetate. For the first two substances, an almost linear increase of the constant is observed up to reactant concentrations corresponding to the concentration of the reactive sulphydryl groups. Next, for phenylmercury acetate, the slope of the curve diminishes, while for benzylmercury acetate it actually increases. The results of the study have been interpreted taking into account the almost complete dissociation of HbCO into dimers at pH 4.0.[42] In the presence of benzylmercury acetate, the acceleration of the oxidation of HbCO after the binding of the reactive SH groups is due to the stronger effect of the reaction leading to the dissociation of the dimers into the monomers. The second break in the curve occurs in the region where the reaction of the reagent with the four SH groups of HbCO is completed. Hence one may conclude that the β-122 SH groups interact stoichiometrically and fairly rapidly with benzylmercury acetate. On the other hand, a further increase of the concentration of the latter is accompanied by a slower increase of the rate constant: in all probability the blocking of the β-112 SH groups does not entail the complete dissociation of the dimers and this process is completed only after the binding of the least accessible α-104 SH groups. A similar curve but with more distinct breaks has been obtained also for methoxycarbonylmercury chloride. In the case of phenylmercury acetate the first break in the curve also indicates the stoichiometric binding of the β-93 SH groups. On the other hand, the subsequent decrease of the slope of the curve and the absence of a break in the region corresponding to the four SH groups suggest the absence of the selective interaction of phenylmercury acetate with the β-112 SH groups. Despite the considerable scatter of the results the curve for mercury acetate (Fig.7) makes it possible to assert that, when account is taken of the "bivalence" of this salt, its effect is comparable in magnitude to that of the "univalent" benzylmercury acetate. On passing from the acetate buffer to the phosphate–citrate buffer, the chelating effect of the citrate in relation to the mercury compounds, inhibiting their activity, was observed. The important role of the reaction temperature, which influences the selectivity of the interaction of the mercury reagent with SH groups of different types has been demonstrated in relation to the oxidation of HbCO in the presence of added benzylmercury acetate[75]. Thus, following an increase of the reaction temperature from 30° to 39 °C at pH 4.0, the break characterising the stoichiometric selective binding of the reactive SH groups disappears, while the break in the region corresponding to the four SH groups is retained. An increase of temperature probably unmasks the β-112 SH groups at pH 4.0 and makes them just as accessible as the β-93 SH groups. Furthermore, it has been observed that at 39 °C the decrease of the pH in the range 4.85–4.0 (acetate buffer) also leads to a decrease of the selectivity of the interaction of benzylmercury acetate with SH groups of different types.

In the study quoted above[67], it was shown by the kinetic method described here that the new stable 4-bromo-2,2,6,6-tetramethyl-4-nitropiperidin-1-yloxy-radical is selectively

bound in alkaline media to the reactive SH groups of HbO_2, hardly altering the rate of autoxidation of HbO_2 but inducing a significant acceleration when it is bound to the unreactive SH groups of HbO_2. A procedure can be proposed for the estimation of the degree of binding and the denaturing effect of the new spin labels.

5. The Autoxidation of HbO_2 in the Presence of Reductants

It is known that the autoxidation of HbO_2 can be accelerated in the presence of reductants. Phenols, hydroquinone[76], phenylhydrazine[77,78], and aniline[78] have been most frequently tried as the latter. The role of the reductants in the oxidation of HbO_2 is usually explained[76] by assuming that the reductant transfers an electron bound by the haem iron to the oxygen, which simultaneously receives an electron from the iron and is reduced (after the binding of two protons) to H_2O_2. It is then also assumed that there is a posibility of two main mechanisms. Firstly, the reductant can interact with O_2^- after its formation, i.e. after the electron transfer from iron to oxygen. In this case the acceleration of the autoxidation of HbO_2 is comparatively slight. The other mechanism presupposes the interaction of the reductant with O_2^- in its formation stage, which is in this case rate-limiting. The reductant then accelerates precisely this stage, which results in an appreciably greater increase of the rate of autoxidation.

It has been observed[80] that the autoxidation of HbO_2 is accelerated also by a biological accelerator—glutathione (G). It has been shown that the formation of Hb^+ in its presence is due to hydrogen peroxide. The latter oxidises HbO_2 much more effectively than glutathione at the same concentration. The rate of formation of Hb^+ is proportional to the square of the concentration of glutathione, which made it possible to put forward the following simplified scheme for the process:

$$2G{-}SH + O_2 \rightarrow G{-}S{-}S{-}G + H_2O_2 ,$$
$$Hb \xrightarrow{H_2O_2} Hb^+ .$$

The influence of hydroquinone and catechol was studied in relation to the autoxidation of sheep and ox HbO_2 [76] in 0.05 M phosphate buffer at pH 6.8 with added EDTA at 37 °C. It was established that both dihydric phenols act catalytically, i.e. can be quantitatively isolated after the completion of the oxidation of HbO_2. In the presence of a tenfold excess of hydroquinone the arrest of the reaction was observed in the first ten or more seconds, which could be eliminated by adding a small amount of *p*-benzoquinone. Next it was observed that, in the absence of hydroquinone, benzoquinone reacts stoichiometrically with HbO_2. Thus in the proposed mechanism the benzoquinone formed initially as a result of the oxidation of hydroquinone oxidises HbO_2 with elimination of oxygen. The semiquinone formed oxidises in its turn a second HbO_2 molecule, which regenerates the benzoquinone. It has been established[81] that the oxidation of HbO_2 by benzoquinone in a phosphate buffer at pH 6.8 proceeds as a second-order reaction. There exists the view[82] that the hydroquinone participating in the oxidation of HbO_2 is first incorporated in the ligand environment of haem, after which two-electron reduction of O_2 takes place with the simultaneous oxidation of the haem iron and the exogenic ligand. The formation of O_2^- in the analogous HbO_2 oxidation reaction in the presence of phenylhydrazine has been demonstrated indirectly: by the reduction of ferricytochrome in the presence of HbO_2 and phenylhydrazine and by the oxidation of epinephrine.

There exist also data for the acceleration of the oxidation of haemoglobin in the presence of ascorbic acid[83], imidazole[83], hydroxylamine[81], and different amines and amides[79].

IV. THE OXIDATION OF HAEMOGLOBIN BY REAGENTS

1. The Oxidation of Haemoglobin in the Presence of Copper(II)

As already mentioned above, bivalent copper ions have an accelerating effect on the autoxidation of HbO_2, which greatly exceeds the effect of other metal ions[33]. The natural question arises whether Cu(II) is involved directly in the oxidation of the iron of HbO_2 in the presence of O_2 [Eqn.(6)] or whether it influences the structure of the protein [Eqn.(7)]:

$$Cu(II) \cdots HbO_2 \rightleftarrows Cu(I) \cdots Hb^+ + O_2 , \quad (6)$$
$$Cu(II) \cdots HbO_2 \rightleftarrows Cu(II) \cdots Hb^+ + O_2^- . \quad (7)$$

The mechanism of the action of Cu(II) has been studied in detail[84] using horse haemoglobin. It has been shown that the autoxidation of the purified HbO_2 at the normal pH is due mainly to traces of Cu(II) in solution. The addition of 10^{-4} M EDTA to 7.2×10^{-5} M HbO_2 sharply inhibits the autoxidation reaction. It has been shown by calculation that, in the absence of EDTA, an appreciable acceleration of the autoxidation is ensured by even 1–2 Cu(II) ions per 1000 haem species [the haemolysate contains 1.7 Cu(II) ions per 1000 haems]. The removal of O_2 from the system simplifies the situation: the entire copper is rapidly reduced quantitatively by the haemoglobin, after which the oxidation of Hb no longer takes place (Fig.8). In the presence of O_2, rapid initial oxidation of HbO_2 also takes place, after which comes the stage in which the oxidation is appreciably slower. The author suggests that the rapid oxidation of HbO_2 is caused by the direct transfer of an electron from Fe(II) in HbO_2 to Cu(II). In the slow stage the same process takes place, but the rate of the stage is limited by the regeneration of Cu(II) and Cu(I) in accordance with the equation

$$4Cu(I) + O_2 + 4H^+ \rightarrow 4Cu(II) + 2H_2O .$$

Comparison of the curves in Fig.8 shows that the rate of the rapid HbO_2 oxidation stage is lower than the rate of oxidation of Hb. This is an argument in support of the preliminary dissociation reaction $HbO_2 \rightleftharpoons Hb + O_2$ with conversion of the *R* form of haemoglobin into the *T* form, which, judging from all the evidence, shows a greater tendency towards oxidation by copper. The virtually complete absence of the oxidation of the weakly dissociated HbCO under these conditions constitutes a satisfactory confirmation of this finding. The question arises why Cu(II) oxidises Hb more effectively than other metal ions having a higher oxidation potential. This might be accounted for by the specific binding of Cu(II) to Hb, which facilitates the electron transfer. The equilibrium dialysis in 0.05 M tris buffer at pH 7.2 with the ratio Cu:haem = 1:2 showed that Cu(II) is bound to Hb, but only to 2 of the 4 subunits. This explains naturally why the degree of oxidation of HbO_2 or Hb presented in Fig.8 does not exceed 50%.

The latter conclusion was confirmed in relation to human haemoglobin[85]. It follows from Fig.9 that, when between two and four Cu(II) ions are transferred to the HbO_2 tetramer, there is a sharp jump in the rate of the rapid oxidation stage. On the other hand, this stage is fully inhibited by the blocking of the β-93 SH groups by iodoacetamides. Thus Cu(II) oxidises only the β-chains of human Hb and HbO_2.

This has been confirmed by the observed inertness of Cu(II) with respect to isolated α-chains, while isolated β-chains (the β_4 tetramer) were oxidised very rapidly. Superoxide dismutase and catalase inhibit the slow stage involving the oxidation of HbO_2 but do not affect the rapid stage. This confirms the direct oxidation of HbO_2 by copper in the rapid stage and the catalytic autoxidation of HbO_2 in the slow stage accompanied by the formation of O_2^- and H_2O_2 in the system.

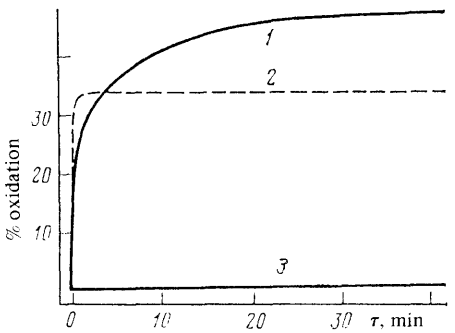


Figure 8. Time variation of the percentage oxidation of 1.42×10^{-4} M solutions of haem derived from horse HbO_2 (curve *1*), Hb (curve *2*), and HbCO (curve *3*) (in the absence of O_2) in a bis–tris buffer (pH 7.0) at 24 °C with added 5×10^{-5} M Cu(II);[84] τ is the time.

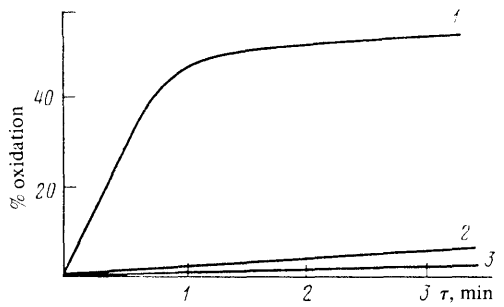
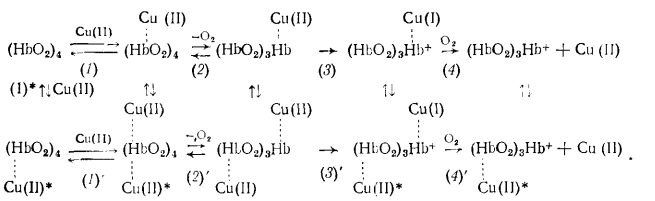


Figure 9. Kinetic curves for the oxidation of HbO_2 by four Cu(II) ions per tetramer (curve *1*), two Cu(II) ions per tetramer (curve *2*), and an excess of Cu(II) in the presence of iodoacetamide (curve *3*);[85] τ is the time.

Dialysis showed that human HbO_2 has four centres for the strong binding of Cu(II). In addition, there are also several (probably two) centres for the weak binding of Cu(II). It has been suggested that the first pair of Cu(II) ions are bound to the β-93 SH groups; the second pair, which ensures the rapid oxidation of HbO_2, is bound to centres located in the vicinity of haem, which ensures the transfer of an electron from Fe(II) to Cu(II) and the formation of haemochrome. The oxidation of the iron in the haem species is followed by the oxidation of the β-93 SH groups with formation of β-dimers containing the disulphide linkage. The presence of these dimers in the reaction product has been observed by gel electrophoresis. The third pair of bound Cu(II) ions are the cause, in the authors' view, of the experimentally observed precipitation of the haemoprotein.

Rifkind et al.[86] failed to confirm the binding of Cu(II) to the β-93 SH groups and also the formation of β-dimers by a procedure involving the modification of HbO_2 by *N*-ethylmaleimide and the comparison of the degrees of binding of Cu(II) to various haemoglobins (human, rabbit, horse, sheep, and bovine haemoglobins). Instead, it was suggested that in the case of human HbO_2 the first two Cu(II) ions are strongly bound to His β-2 or β-116 located on the proximal side in relation to haem and at a fairly long distance from it. At the same time, these residues are located close to the β-93 SH groups and the modification of the latter influences the binding of Cu(II) to His β-2 or β-116. Fig. 10 presents for comparison curves for the oxidation of horse and human HbO_2 as a function of the Cu(II) concentration. The indistinct break in the curve for human HbO_2 in the presence of 0.5 of a Cu(II) ion per haem moiety indicates the competitive binding of Cu(II) to the first and second pairs of centres for the binding of Cu(II). A scheme incorporating individual stages in which Cu(II) is bound and HbO_2 oxidised has been proposed:



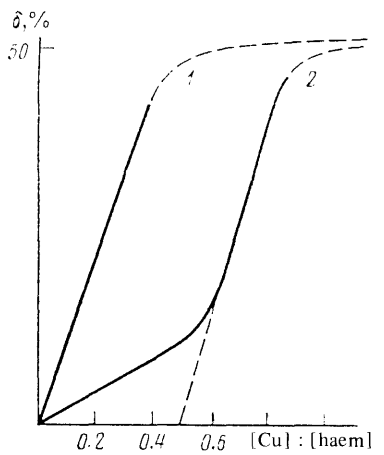


Figure 10. Dependence of the percentage of HbO_2 oxidised in the rapid stage (δ) on the amount of added Cu(II):[86] *1*) horse HbO_2; *2*) human HbO_2.

Stages (1)–(4) obtain in the case of horse HbO_2. For human HbO_2, stages (*1'*)–(*4'*) compete with the above stages. It follows from the scheme that in the latter case HbO_2 without a strongly bound Cu(II) ion can also participate in the haem iron oxidation step (stages marked by an asterisk).

It has been observed[87] that, in contrast to human and horse HbO_2 and Hb, in the sheep haemoglobins Cu(II) rapidly oxidises the haem moieties not only in the β-subunits

but also in the α-subunits. The experiments were performed at pH 6.9 in the absence of buffer in order to prevent the formation of Cu(II) complexes which might influence the mechanism of the action of this ion. The activation energies have been calculated as 53 kJ mol^{-1} for HbO_2 and 113 kJ mol^{-1} for Hb.

We shall consider in greater detail the study already mentioned, where the mechanism of the oxidation of sperm whale myoglobin by copper(II) was investigated[34]. The initial rate of oxidation of MbO_2 was determined spectrophotometrically (at $\lambda = 542$ nm) from the decrease of its concentration. It was shown that in an acid medium the kinetics of the oxidation of MbO_2 are more sensitive to the presence of Cu(II). Thus a change in the MbO_2:Cu(II) ratio from 1:0.125 to 1:12 increases the rate of reaction by a factor of ~45 at pH 5 and only by a factor of ~15 at pH 7. The steepness of the relations between the logarithm of the rate of reaction and $1/T$ in the temperature range 10–30 °C increases with decrease of pH. The authors explained this by the fact that the interaction of Cu(II) with the His GH1 centre for the binding of Cu(II), which is charged at low pH, leads to local changes unfavourable for electron transfer from haem to this centre, while an increase of temperature eliminates these difficulties. The sharp break in the relation at 30 °C (at temperatures in the range 30–40 °C the relation has much lower slopes, particularly at pH 6 and 7) is explained by a change in the hydration shell of the protein at this temperature. The authors compared the mechanisms of the autoxidation of MbO_2 and the oxidation of MbO_2 by copper(II). In the former case electron transfer via the protein to the O_2 dissolved in the medium as the final acceptor is postulated together with the simple splitting off of O_2^-. In the oxidation by Cu(II) the Cu(II) itself acts as such an acceptor. The electron transfer to copper requires the delocalisation of the electron of haem iron involving the tentative centre for the binding of Cu(II), namely His GH1. The probability of finding an electron in this centre depends on the degree of its protonation. The Cu(II) cation acts analogously—by being bound to His GH1 it increases the positive charge on the histidine, which increases the probability that an electron enters this region. The authors also postulate a mechanism in which Cu(II) is a centre for the binding of the dissolved O_2 acceptor. In this case the Fe(II)...Cu(II)... O_2 electron transfer chain with increasing redox potential may arise, as a result of which the electron transfer becomes thermodynamically spontaneous.

2. The Oxidation of Haemoglobin by Potassium Hexacyanoferrate(III)

The oxidation of haemoglobin and myoglobin by potassium hexacyanoferrate(III) constitutes the usual method of obtaining the oxidised forms of both haemoproteins. Despite this, almost no systematic studies of the kinetics and mechanisms of these reactions have been described in the chemical literature. It is therefore useful to consider only one study, by Antonini et al.[88], in which both of the above human haemoproteins were investigated. It was shown that the simpler system (Mb) reacts with potassium hexacyanoferrate(III) strictly in accordance with a second-order mechanism. $\Delta H^{\neq} = 4$ at pH 6 (0.1 M phosphate buffer) and $\Delta H^{\neq} = 0$ at pH 9.2 (borate buffer). It has been suggested that MbO_2 interacts with hexacyanoferrate(III) only after the dissociation reaction $MbO_2 \rightleftharpoons Mb + O_2$. In this case the rate of oxidation of MbO_2 should be determined either by the rate of its dissociation into Mb and O_2 or by the rate of reaction of Mb with O_2 and hexacyanoferrate(III). A linear relation between the reciprocal of the rate constant and the O_2 concentration in solution was observed at pH 6, which shows that the rate-limiting stage in the process is the dissociation of MbO_2. However, at pH 9.2 the linearity of the above relation no longer holds, which indicates deviations of the process mechanism at pH 9.2 from the simple dissociative scheme. The authors explained the influence of pH on the reaction by its effect not on MbO_2 but on hexacyanoferrate on the grounds that the influence of pH had not been observed in ligand substitution reactions involving MbO_2 (for example, reactions with CO), which have much in common with the reaction involving hexacyanoferrate(III).

When an excess of hexacyanoferrate(III) was allowed to interact with Hb, the first-order rate constant varied linearly during the reaction: it increased by a factor of 1.5 at pH 9.2 and decreased by a factor of 2 at pH 6.45, which was explained by the non-equivalence of the α- and β-chains in Hb. An increase of pH from 6.0 to 9.2 reduced by an order of magnitude the initial rate of reaction. In all cases the rate of oxidation of Hb remained ~100 times lower than the rate of oxidation of Mb under these conditions. The observation that hexacyanoferrate(III) does not oxidise the sulphydryl groups in Hb is significant: the addition of EDTA, which inhibits the oxidation of these groups, did not alter the rate of reaction.

The necessity for the preliminary dissociation into Hb and O_2 is postulated for the reaction of hexacyanoferrate(III) with HbO_2 as well as MbO_2, which was also confirmed by the increase of the rate of oxidation of HbO_2 as the partial pressure of O_2 in the mixture is reduced at pH 6.1 and 9.1 {18 °C, $[HbO_2]_0 = 10^{-5}$ M, and $[K_3Fe(CN)_6]_0 = 5 \times 10^{-3}$ M}.

There exist data concerning the products of the oxidation of horse Hb by hexacyanoferrate(III).[89] It was established by the method of isoelectric focussing that the β-chains are oxidised preferentially. However, a decrease of the ionic strength of the solution (to 0.001 M phosphate) accelerates the oxidation of the α-chains. On the other hand, the addition of inositol hexaphosphate, Cl^-, and the phosphate anion intensifies the oxidation of the β-chains.

3. The Oxidation of Haemoglobin by Nitrite

A much greater number of special investigations have been devoted to the oxidation of haemoglobin by nitrite than to its oxidation by hexacyanoferrate(III). This is apparently because poisoning by nitrite is not rare under modern hygienic conditions. Nitrite contaminates food particularly frequently by being present in water, the sources of which it enters in its turn from the soil[90].

While the mechanism of the reactions of haemoproteins with potassium hexacyanoferrate(III) is relatively simple and at least remains constant during a particular reaction, this cannot be said of the reactions of haemoproteins with nitrite. The most significant characteristic feature of the reaction HbO_2 with nitrite in its autocatalytic character: the kinetic curve is S-shaped (Fig.11). It has been observed[91] that the rate of oxidation of human HbO_2 by nitrite is proportional to $[NaNO_2]^{1.4}$. This reaction order is determined wholly by the structure of the protein, since in the case of rat HbO_2 the order with respect to nitrite is 3–4. Bearing in mind that a decrease of pH from 7.5 to 5.5 entails a linear decrease of the logarithm of the reaction half-life, i.e. that the rate of reaction increases with increase of the activity protons, the authors suggest that the reaction rate depends on the concentration of undissociated HNO_2. At the same time they do not take into account the fact that an increase of the

acidity of the medium always promotes denaturation processes, which have a particularly accelerating effect on the oxidation of HbO_2. Nevertheless, the reality of the increase of the HNO_2 concentration as the pH is reduced to 5.5 must be taken into account and the possible process mechanisms must be considered (HNO_2 can serve, for example, as a source of NO). Next the authors[91] discussed in detail the probability of the involvement of particular system components in the autocatalysis. Special experiments showed that Hb^+ does not influence the rate of reaction and it cannot therefore be the autocatalyst. The same was also established for the possible decomposition products of nitrous acid and also for nitrate. It may be that the autocatalytic character of the reaction is due to the accumulation of hydrogen peroxide in the system, which has been found to shorten the induction period. However, the inertness of H_2O_2 in the subsequent stages of the reaction led the authors to doubt its autocatalytic effect.

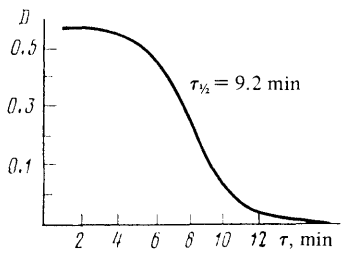


Figure 11. Kinetic curve for the oxidation of HbO_2 by nitrite; $[HbO_2]_0 = 1.8 \times 10^{-5}$ M, $[NaNO_2]_0 = 1.45 \times 10^{-3}$ M; 0.05 M bis–tris buffer at pH 7.0 with 0.1 M NaCl at 25 °C;[100] *D* is the optical density at 578 nm.

The above study[91] was continued by the investigation of the formation of methaemoglobin *in vivo* by administering sublethal amounts of $NaNO_2$ to dogs and rats[90]. After dogs had been administered perorally up to 20 mg of $NaNO_2$ per kilogram of body weight, an increase of the Hb^+ concentration in the blood of the animals was observed in the course of ~30 min up to a concentration of 25%, followed by a slow fall. At the same time EPR showed that in the initial stage of the intoxication process the HbNO concentration rises rapidly and reaches 2% after 10 min and then falls relatively fast. The authors explained the appearance of HbNO by the reduction of the unstable complex Hb^+NO, formed during intoxication, by reductase systems. The possibility of the formation of Hb^+NO enabled the authors to put forward the following mechanism of the oxidation of haemoglobin by nitrite:

$$Fe_p^{2+} + NO_2^- \rightarrow Fe_p^{2+} - NO_2^- ,$$
$$Fe_p^{2+} - NO_2^- + 2H^+ \rightarrow Fe_p^{3+} - NO^+ + H_2O ,$$
$$Fe_p^{2+} - NO^+ \rightleftarrows Fe^{3+} - NO ,$$
$$Fe_p^{2+} - NO + H_2O \rightleftarrows Fe_p^{3+} - H_2O + NO .$$

The second stage explains the observed[91] pH dependence of the oxidation of HbO_2 by nitrite. Stage 3, which is generally speaking fictitious, since it actually indicates only the presence of two resonance structures with Fe(II) and Fe(III), formally demonstrates the mechanism of the oxidation of iron, such oxidation being observed after the substitution of the NO ligand in Fe_p^{3+}–NO by water.

A more elaborate mechanism of the oxidation of HbO_2 by nitrite has been postulated by Tomoda et al.[92]. Bearing in mind that nitrite (like dithionite) is a reductant for O_2, the authors suggested that it interacts with the O_2 bound to iron and generates O_2^-. Experiment confirmed this hypothesis: the introduction of exogenic O_2^- into the system shortened the induction period of the oxidation reaction and the addition of superoxide dismutase lengthened it. The presence of $(\alpha^{O_2}\beta^+)_2$ and $(\alpha^+\beta^{O_2})_2$ was detected by the method involving the isoelectrofocussing of the partly oxidised HbO_2. Taking these two species into account, the process mechanism assumes the following form [Int $Hb(O_2)_2$ represents different half-oxidisied HbO_2 species]:

$$Hb(O_2)_4 + 2NO_2^- \rightarrow Int\,Hb(O_2)_2 + 2NO_3^- + O_2^- ,$$
$$2NO_2^- + 2O_2^- + 6H^+ \rightarrow 2NO + H_2O_2 + 2H_2O + O_2 ,$$
$$Hb(O_2)_4 + 2NO \rightarrow Int Hb(O_2)_2 + 2NO_2^- + O_2^- ,$$
$$Int Hb(O_2)_2 + 2NO_2^- \rightarrow Hb^+ + 2NO_3^- + O_2^- ,$$
$$2NO_2^- + 2O_2^- + 6H^+ \rightarrow 2NO + H_2O_2 + 2H_2O + O_2 ,$$
$$Int\,Hb(O_2)_2 + 2NO \rightarrow Hb^+ + 2NO_2^- + O_2^- .$$

Thus

$$Hb(O_2)_2 + 2NO_2^- + 6H^+ \rightarrow Hb^+ + 2NO_3^- + H_2O_2 + 2H_2O + O_2 ,$$
$$2O_2^- + H_2O_2 \rightarrow 2H^+ + 2NO_3^- ,$$

or ultimately

$$Hb(O_2)_4 + 4NO_2^- + 4H^+ \rightarrow Hb^+ + 4NO_3^- + 2H_2O + O_2 .$$

The final product of the oxidation of haemoglobin by nitrite has aroused particular interest among investigators. It has been noted[93] that, although the absorption spectra of the Hb^+ solutions formed on oxidation of HbO_2 by nitrite and hexacyanoferrate(III) have the same maximum at 630 nm, in other regions the spectra differ appreciably. The main difference between the nitrite Hb^+ is the presence of a distinct maximum at 540 nm. The hexacyanoferrate(III) Hb^+ has a maximum at 504 nm. The specific spectroscopic characteristics of the nitrite Hb^+ made it necesssary to assume[94] that nitrite oxidises the haem iron and at the same time reacts irreversibly with the protein or with the porphyrin. It was then claimed that the above reactions do not entail significant changes in the Hb^+ structure. The following experiment was carried out to demonstrate the irreversibility of the reaction of HbO_2 with nitrite: Hb^+ which had not been treated with nitrite beforehand was made to react with $NaNO_2$, whereupon NO_2^- was bound to Hb^+ in accordance with a sigmoidal relation; after the dialysis of the product combined with the ligand, it was again treated with nitrite and in this instance the NO_2^- was bound in accordance with a hyperbolic relation. The application of the EPR method[95] demonstrated the paramagnetic nature of the intermediate products of the oxidation of HbO_2 by nitrite. The formation of paramagnetic centres with $g = 2.005$ as well as the oxidation itself were characterised by an induction period and were accelerated with increase of the concentration of nitrite and with decrease of pH. The maximum of the EPR signal corresponded to a break in the Hb^+ formation curve. The EPR signal detected characterises the paramagnetic centres which exhibit autocatalytic activity and are not bound directly to NO. However, in a recently published study[96] it is claimed that prolonged dialysis of the Hb^+ solutions obtained by oxidising HbO_2 and Hb by nitrite and hexacyanoferrate(III) leads to the disappearance of spectroscopic differences betwee Hb^+ of different origin. This enabled the authors to assume that the conformations of Hb^+ are identical in the two cases, which rules out the hypothesis of the oxidation of the protein or the porphyrin fragment in

either procedure for the oxidation of haemoglobin. It is remarkable that the idea of the non-identity of the nitrite and hexacyanoferrate(III) Hb^+, allegedly associated with the different rates of their reduction by ascorbic acid[97], was disproved as early as 1943 [98] after experiments involving 24 h dialysis of the hexacyanoferrate(III) Hb^+ containing, before dialysis, residual potassium hexacyanoferrate(II), which accelerates the reduction of Hb^+.

As noted above[88], whereas hexacyanoferrate(III) oxidises Hb faster than HbO_2, the opposite behaviour obtains in the reaction with nitrite: Hb is not oxidised by nitrite at all[99]. The idea naturally arose that the allosteric effectors which reduce the affinity of Hb for O_2 should inhibit the oxidation of HbO_2 by nitrite. This hypothesis was confirmed in experiments with added inositol hexaphosphate[100]. The latter eliminated almost completely the rapid stage of the process, which follows the induction period. The mechanism of the action of inositol hexaphosphate, which presuposes the conversion of the *R* conformation of haemoglobin into the *T* conformation, has been satisfactorily confirmed by the accelerating influence of this effector on the oxidation of HbO_2 by hexacyanoferrate(III). However, later data[101] showed that other powerful allosteric effectors (DPG, NADP, and ADP) present in 2 and 5 molar excess do not affect the rate of oxidation of Hb by nitrite. It was concluded that the effect of inositol hexaphosphate observed previously is due to some factor other than the $R \rightarrow T$ transition.

The reactive SH groups play a special role in the oxidation of HbO_2 by nitrite[101]. It has been established that the blocking of these groups by iodoacetamide eliminates the inhibiting effect of inositol hexaphosphate for HbO_2 but causes no changes in the case of Hb.

V. THE OXIDATION OF HAEMOGLOBIN UNDER THE INFLUENCE OF RADIATION

In 1927 Fricke and Peterson[102] showed that, in the radiolysis of solutions of HbO_2, the latter undergoes partial oxidation. Manoilov devoted a number of studies to the action of ionising radiation on haemoproteins. He is the author of a review[103] which discusses, in particular, his work and that of other investigators on the oxidation of haemoglobin under the influence of radiation. In view of the existence of this review and also that of Starodub et al.[104], we shall consider only briefly certain studies, which give an idea about this research field and the main results achieved.

In order to understand the causes of the oxidation of haemoglobin, it is important to know the different characteristic changes occurring when solutions are irradiated. In particular a decrease of the redox potential of human haemoglobin has been observed in the course of γ-irradiation[105]. For a dose of 10–100 krad, the changes in the redox potential are slight. The potential falls by 10 mV at 500 krad and by 45 mV at 4.75 krad. The oxidation of HbO_2 on γ-irradiation of its solutions with doses in excess of 1 Mrad is accompanied by a change in the sedimentation coefficient and in the viscosity of the solution[106]. For doses greater than 4–5 Mrad, the appearance of haemochromogen was noted. During irradiation, the affinity of some of the haemoglobin molecules for O_2 increases and the haem–haem interactions are weakened. As stated above[30], these facts characterise the appearance in the solution of partly oxidised forms of haemoglobin.

γ-Irradiation can change from a factor promoting the oxidation of haem iron to one which causes reduction when Hb^+ solutions are irradiated. The solvated electron has been postulated as the primary reducing agent[107,108]:

$$Hb(Fe^{3+})_4 + e^-_{aq} \rightarrow Hb(Fe^{3+})_3(Fe^{2+}).$$

Hb^+ is also reduced on γ-irradiation of its frozen solutions at 77 K.[109] The difference between the optical spectra of the reduced Hb^+ and that of the usual Hb justifies the hypothesis of the formation during the reduction process of an active centre in a low-spin state, the centre being atypical for Hb.

The effects observed in the γ-irradiation of haemoglobin solutions are to a large extent characteristic also of irradiation by X-rays. It has been noted[110] that the stage of the haemoglobin oxidation proper is preceded by a stage in which O_2 is abstracted from HbO_2. The deoxy-form formed resembles the known product of the photodissociation of HbO_2. The Hb^+ arising during irradiation is in a high-spin state. For an irradiation dose of 10–100 krad, a decrease of the redox potential has been noted[111].

Haemoglobin is also oxidised during photoirradiation. During the exposure of an aqueous solution of mouse HbO_2 at 20–50 °C and pH 6.0 to the ultraviolet light of the PRK-4 lamp, the degree of oxidation of haemoglobin increases with the irradiation dose[112]. Under anaerobic conditions there is no oxidation. It has been suggested that the oxidation is preceded by the rupture of the haem–haemoglobin bond.

The damage to haemoglobin during irradiation can therefore be one of the links in the general radiation pathology of the animal organism[103].

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During the preparation of this review for the press, studies on the autoxidation of haemoglobins and myoglobins[113–115], on the oxidation of HbO_2 by phenylhydrazine[116] and nitrofurantoin[117], on the oxidation of haemoglobins by nitrites[118–121], and on the oxidation of sulphhaemoglobin by hexacyanoferrate(III) [122] were published.

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Institute of Chemical Physics,
USSR Academy of Sciences, Moscow

Russian Chemical Reviews

July 1984

Translated from *Uspekhi Khimii*, 53, 1073-1100 (1984)

U.D.C. 541.124

Kinetics of the Recombination of Radicals and Radical-ions in the Liquid Phase

Kh.S.Bagdasar'yan

The present state of the theory of the recombination of radicals and radical-ions is described on the basis of the diffusion gradient approach and in terms of the approximation of homogeneous chemical kinetics. The experimental data on the cage effect and on the kinetics of the geminate and volume recombination of radicals and radical-ions are discussed within the framework of the methods indicated. Particular attention is devoted to the influence of the viscosity of the medium on these processes. Spin effects in radical and radical-ion pairs and their influence on the recombination kinetics in the absence and presence of an external magnetic field are considered.
The bibliography includes 61 references.

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I. INTRODUCTION

The recombination of radicals (radical-ions) in the liquid phase is a complex reaction of a special type. The rate of recombination and the composition of the products are determined by the competition between several elementary processes. The complexity of this reaction follows directly from the significant difference between the reactions in the gas and liquid phases. In gases the reaction proceeds on collisions between the molecules; after each collision, the molecules either react or move apart to distances greatly exceeding the molecular diameters, after which collisions take place with other molecules. In the liquid phase chemical reactions proceed on encounters between molecules, which leads to the formation of a "pair" surrounded on all sides by the molecules of the liquid. The pair is characterised by an intrinsic lifetime or a dissociation rate constant. If there is no specific interaction between the molecules of the pair, then its lifetime is determined solely by the molecular movement and is of the order of R^2/D, where R is the sum of the molecular radii and D the sum of the diffusion coefficients. For the usual liquids ($D \cong 2 \times 10^{-5}$ cm^2 s^{-1} and $R \cong 5 \times 10^{-8}$ cm), the lifetime of the pair is $\sim 10^{-10}$ s. In viscous media or in a specific interaction between the molecules of the pair, its lifetime can be much greater.

If a potential barrier of the usual magnitude ($\geq$25 kJ mol^{-1}) exists for the given reaction and there is no specific interaction between the members of the pair, then during the lifetime of the latter the probability of the reaction is very low. In this case the kinetics of the liquid-phase reactions can be considered employing the usual methods of homogeneous chemical kinetics and the concept or pairs becomes superfluous. If there is no potential barrier for the reaction or it is very small, then the rate of such a reaction in the liquid phase can

be represented by the product of the rate of formation of the pairs and the probability of the reaction within the pair. The recombination of radicals (radical-ions) belongs to this class of reactions, which will be the subject of the present review.

Radical pairs are formed not only in the encounters of radicals but they also arise in the primary chemical step. The thermal or photochemical decomposition of molecules into atoms or radicals leads to the formation of a primary or geminate radical pair. Electron transfer from one molecule to another leads to the formation of a geminate radical-ion pair. The photo-ionisation of a molecule with ejection of an electron into the liquid medium results in the formation of a geminate radical-cation–electron pair. The geminate pairs either recombine (geminate recombination) or dissociate with liberation of the two species involved into space. Competition between these processes has come to be called the "cage effect". The radicals released into space react with radical acceptors or solvent molecules, forming secondary radicals. Ultimately all the radicals recombine via the formation of pairs in encounters.

An important characteristic of radical pairs is their spin state. The radical pair undergoes a periodic evolution of its spin state. In the simplest case there is a transition from a purely singlet state (the spins of the unpaired electrons of the radicals pair are antiparallel) to a purely triplet state (the spins of the unpaired electrons are parallel) and conversely via a continuous sequence of mixed states†. A radical pair can recombine only in the singlet state while a radical-ion pair can recombine (reverse electron transfer) also in the triplet state with formation of an electron donor or acceptor molecule in the triplet state. The spin evolution can take place under the influence of an external magnetic field, but is also possible without such a field as a result of the interaction of the unpaired electron with the paramagnetic nuclei of the radical, for example, with protons. The spin evolution and the factors influencing it lead to interesting phenomena such as the chemically induced nuclear polarisation, the influence of the magnetic field on chemical reactions, the magnetic isotope effect, and chemical radioemission. All these phenomena as well as the macroscopic recombination kinetics, the composition of the recombination products, the effectiveness of the initiation of radical chain reactions, and the effectiveness of photochemical systems for the transformation of light (solar) energy are determined by elementary processes involving a radical (radical-ion) pair, i.e. the recombination, dissociation, and spin transformations of the pair.

The difficulty of the theoretical analysis of barrier-free chemical reactions in the liquid phase is associated with the need of a detailed knowledge of the rules governding the molecular movement in liquids and solutions. The simplest version of this approach is the method of molecular pairs (Noyes[1]), according to which the molecules (radicals) of the pair are involved in a series of successive encounters as a consequence of molecular movement. The time between the encounters is defined by a semiempirical formula proposed by Noyes.[1] In each encounter the reaction takes place with a certain probability. The method based on the familiar relation between the disordered character of the molecular movement and diffusion—the macroscopic manifestation of this movement—has come to be widely used. This approach has been called the method of the diffusion gradient or diffusion kinetics. Subsequently we shall make use of the simplest versions of the method of diffusion kinetics. We may also note that the Noyes method has no advantages over the diffusion gradient method, as can be seen from their comparison,[1,2] and futhermore it is inconvenient for the consideration of complex kinetics. In this case the diffusion gradient method can be used in terms of the approximation of chemical kinetics, as will be described in the present review.

II. RADICAL PAIRS

1. Kinetics of the Formation and Dissociation of Radical Pairs

A radical pair is an intermediate short-lived species in radical reactions and its behaviour determines both the kinetics and the chemistry of radical reactions. We shall consider the kinetics of the formation of radical pairs in the encounters of radicals.

In 1918 Smoluchowski[3] considered the kinetics of fast coagulation on the basis of the following model. Small particles are linked to a large particle with a radius R, the size of the former being negligible compared with that of the large particle. The small particles do not interact with one another but disappear following each contact with the large particle. The rate of disappearance (adhesion) of the small particles is determined by the diffusion flux Φ of the small particles to the surface of the large particle:

$$\Phi = 4\pi R^2 D \left| \frac{\mathrm{d}c}{\mathrm{d}x} \right|_R , \qquad (1)$$

where D is the diffusion coefficient of the small particles and $|\mathrm{d}c/\mathrm{d}x|_R$ the concentration gradient of the small particles at the surface of the large particle. The concentration gradient is found by solving the diffusion equation

$$\frac{\partial c}{\partial t} = \frac{D}{x} \frac{\partial^2 (cx)}{\partial x^2} \qquad (2)$$

subject to the initial condition $c(0, x) = c_\infty$ (a uniform distribution of the small particles throughout the entire volume in the initial instant) and the boundary conditions $c(t, R) = 0$ (adhesion following each contact, so that $c = 0$ on the surface of the particle with a radius R) and $c(t, \infty) = c_\infty$ (constant concentration in the region remote from the surface). Expressions for the concentration gradient at the boundary of the large particle,

$$\left| \frac{\mathrm{d}c}{\mathrm{d}x} \right|_R = \frac{c_\infty}{R} [1 + R (\pi D t)^{-1/2}] , \qquad (3)$$

and for the diffusion flux,

$$\Phi = 4\pi R D [1 + R (\pi D t)^{-1/2}] c_\infty , \qquad (4)$$

which determines the rate of adhesion of the small particles to the large particle, follow from the solution of the diffusion equation. It follows from Eqn.(3) that the concentration gradient of the small particles diminishes continuously as those nearest to the surface adhere to it and, after a time of the order of R^2/D, it reaches the constant value c_∞/R. Correspondingly the diffusion flux also reaches a constant value:

$$\Phi = 4\pi R D c_\infty . \qquad (5)$$

In the studies of Vavilov and co-workers,[4] starting from 1928, the diffusion kinetics were first used to describe a molecular process—the quenching of fluorescence. The application of the method of diffusion kinetics to molecular

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†The concept of the parallel and antiparallel arrangement of spins in the triplet and singlet states is simplified. Strictly speaking, in the triplet state the electron spins are added together, while in the singlet state they are subtracted.

processes is possible on the basis of the following clear model corresponding to Smoluchowski's theory for the coagulation of colloids.[5] One considers the diffusion of non-interacting point particles in the direction towards a sphere (or away from the sphere) with a radius R (the sum of the molecular radii). The sum of the diffusion coefficients of real molecules is adopted as the diffusion coefficient of the point particles. Depending on the character of the problem, the initial and boundary conditions for the point particles are established. The diffusion flux Φ of the point particles to a sphere with a radius R, subject to the boundary conditions indicated above, is identical with the number of encounters per unit time of real molecules A with a single molecule B and Eqns.(4) and (5) correspond to the non-stationary and stationary cases#. The quantity Φ/c_∞ has the dimensions of a bimolecular rate constant and has been called the "time-dependent rate constant". When a stationary regime is established, this quantity represents the bimolecular rate constant for the formation of pairs. If the two radicals are identical, then the multiplier 1/2 must be introduced into Eqns.(5).

An expression for the rate constant for the dissociation of a contact radical pair can be obtained analogously.[6] For this purpose, it is necessary to solve the diffusion equation subject to the initial condition $c(0, x) = 0$ (at the initial instant the point particles are absent from the given volume) and the boundary condition $c(t, R) = c_0$ (a constant concentration of the point particles is maintained at the boundary of a sphere with a radius R). The solution is

$$k_d = \frac{\Phi}{c_0} = \frac{D}{R^2}\left[1 + R(\pi Dt)^{-1/2}\right], \qquad (6)$$

where Φ is the diffusion flux of the point particles away from the surface of a sphere with a radius R into space.

Up to a time of the order of R^2/D, a constant flux is established with a stationary rate constant for the dissociation of the pairs $k_d = D/R^2$.

Stationary expressions for the rate constant for the formation of pairs ($4\pi RD$) and the rate constant for the dissociation of pairs (D/R^2) lead to the kinetic condition for the diffusion equilibrium:

$$4\pi RD[A][B] = \frac{D}{R^2}[AB]_{eq}. \qquad (7)$$

The equilibrium concentration of pairs $[AB]_{eq}$ is determined by the probability that the molecule B enters a spherical layer with a volume $4\pi R_A^2 R_B$. Assuming that the radii of the molecules A and B are identical, we obtain

$$[AB]_{eq} = 4\pi R^3[A][B], \qquad (8)$$

which agrees with the kinetic Eqn.(7) for the diffusion equilibrium.

2. Kinetics of the Recombination in Space

The kinetics of the recombination of radicals without taking into account explicitly the spin state of the radical pair arising following the encounter of the radicals in space are considered in this Section. The kinetic consequences of the spin state of the radical pair will be considered below.

If the reaction takes place in each encounter of the molecules A and B, then the rate of reaction is equal to the rate of formation of the pairs. Having divided Eqn.(5) by c_∞, we obtain an expression for the bimolecular rate constant at the stationary state:

$$k_{diff} = 4\pi RD. \qquad (9)$$

The Stokes–Einstein formula makes it possible to express RD in terms of T/η, where T is the temperature and η the viscosity of the medium; the ratio T/η is called the fluidity of the medium. If the molecular radii are equal, then

$$RD = \frac{4kT}{6\pi f\eta}, \qquad (10)$$

where k is the Boltzmann constant and f a correction factor of the order of unity§. Having substituted Eqn.(10) in Eqn.(9), we obtain an expression for k_{diff} known in the literature as the Smoluchowski–Debye formula:[7]

$$k_{diff} = \frac{8kT}{3f\eta}. \qquad (11)$$

Eqn.(11) had been derived earlier by Vavilov.[8]

We shall now consider a more general case of diffusion kinetics, where not every encounter of the radicals leads to reaction. In this case the concentration of the point particles on the surface of a sphere with a radius R is not zero but has a finite value, which varies during the reaction, tending to a constant. The solution of the diffusion Eqn.(2) leads in this case to the equation (see, for example, Noyes[1])

$$\Phi = \frac{4\pi RDc_\infty}{1 + 4\pi RD/k_2}\left(1 + \frac{k_2}{4\pi RD}e^{z^2}\operatorname{erfc} z\right), \qquad (12)$$

where k_2 is the bimolecular recombination constant not limited by diffusion (see below) and

$$z = \frac{(Dt)^{1/2}}{R}\left(1 + \frac{k_2}{4\pi RD}\right); \quad \operatorname{erfc} z = \frac{2}{\pi^{1/2}}\int_z^\infty e^{-u^2}du.$$

Different special solutions can be obtained from Eqn.(12). If the rate of reaction is limited by diffusion, i.e. $k_2 \gg 4\pi RD$, then $z \to [(Dt)^{1/2}/R](k_2/4\pi RD) \gg 1$ and $e^{z^2}\operatorname{erfc} z \cong 1/\pi^{1/2}z$ (the first term of the expansion of the expression $e^{z^2}\operatorname{erfc} z$ in series for large values of z). We obtain as a result Eqn.(4). It follows from Eqn.(12) that, after a time greater than R^2/D, a stationary flux and a stationary reaction rate are established. In this case [$t \to \infty$, $z \to \infty$, and the expression in brackets in Eqn.(12) tends to unity], we obtain for the experimental bimolecular rate constant k_{exp} the following expression:

$$k_{exp} = \frac{\Phi}{c_\infty} = \frac{4\pi RDk_2}{k_2 + 4\pi RD}. \qquad (13)$$

This important equation can be obtained immediately by formulating an equation for the diffusion flux Φ of point particles through any spherical surface $4\pi x^2$. This stationary flux is independent of x, i.e. Φ is a constant quantity and is found by solving the following equation:

$$\Phi = 4\pi x^2 D\frac{dc}{dx}. \qquad (14)$$

#In theoretical studies by the diffusion gradient method, the term "probability density" of the observation of molecules at a given site and at a given time is employed. The concentration of point particles is a clear expression of the "probability density".

§For simplicity we shall henceforth use Eqn.(10). If the molecular radii are not equal, then an additional multiplier enters Eqn.(10). For example, if the molecular radii differ by a factor of 2, the multiplier is 1.125; it enters into the correction factor f, which effectively characterises the deviation of the behaviour of real molecules from the Stokes–Einstein formula.

(Boundary conditions:

$$x\to\infty,\ c\to c_\infty;\ x\to R,\ c\to c_0,$$

where c_0 is the stationary concentration of the point particles at the surface of a sphere with a radius R). The integration of Eqn.(14) yields the following expression for the diffusion flux at the boundary of a sphere with a radius R:

$$\Phi = 4\pi RD(c_\infty - c_0) \quad . \tag{15}$$

The flux represents the rate of reaction of all the particles A with a single particle B; consequently $\Phi = k_2 c_0$. Thus it is possible to eliminate c_0 from Eqn.(15) and obtain Eqn.(13).

Two limiting cases follow from Eqn.(13).

1. The diffusion flux limits the rate of reaction, i.e. $4\pi RD \ll k_2$; then $k_{exp} = 4\pi RD = k_{diff}$, which agrees with Eqn.(9). For the usual liquids, k_{diff} is a quantity of the order of 10^{10} litre mol^{-1} s^{-1}.

2. The diffusion flux does not limit the rate of reaction, i.e. $4\pi RD \gg k_2$. Then k_2 is identical with the experimental constant k_{exp}. The constant k_2 is sometimes identified with the bimolecular rate constant for the reaction of the same radicals in the gas phase (see below).

It must be emphasised that, regardless of the reason why not every encounter between the radicals leads to reaction (steric hindrance, spin restrictions, or other causes), the diffusion gradient method leads to Eqn.(13) and all the factors hindering reaction determine the constant k_2. We may also note that Eqn.(9) has a limited range of applicability (see Section 6). However, as a consequence of a certain indefiniteness of the concept of the "sum of radii" and also as a consequence of the application of Eqn.(11) instead of Eqn.(9), it is frequently impossible to decide on the basis of experimental data which equation is valid—Eqn.(13) or (9). If the bimolecular recombination rate constant is measured over a wide range of fluidities of the medium, then Eqn.(13) makes it possible to obtain important information about the elementary processes determining the diffusion recombination kinetics (see below).

The concept of pairs was not used in the derivation of Eqn.(13). The experimental recombination constant k_{exp} can be represented as the product of the rate constant for the formation of pairs and the probability ϕ of reaction in the pair:

$$k_{exp} = 4\pi RD\varphi \quad . \tag{16}$$

One should bear in mind that ϕ is not simply a number less than unity but is a dimensional function of a series of kinetic parameters. It follows from Eqns.(13) and (16) that

$$\varphi = k_2/(k_2 + 4\pi RD).$$

On the other hand, ϕ can be expressed in terms of unimolecular constants for the recombination of the pair (k_1) and its dissociation (k_d). We thus obtain the expression

$$\varphi = k_2/(k_2 + 4\pi RD) = k_1/(k_1 + k_d). \tag{17}$$

The stationary rate constant for the dissociation of the pair is equal to D/R^2, which leads to a relation between the bimolecular constant k_2 and the unimolecular pair recombination constant k_1:

$$k_2 = 4\pi R^3 k_1 \quad . \tag{18}$$

In the general case the constant k_1 has a simpler physical significance than the constant k_2.

3. The "Cage Effect" (Stationary Recombination of Geminate Pairs)

One of the manifestations of the diffusion kinetics of the recombination of radicals is the "cage effect". Frank and Rabinovich[9] observed that the quantum yield of the dissociation of a molecule into atoms or radicals in a liquid medium is smaller than in a gaseous medium. This was explained by the fact that the radicals formed on dissociation are surrounded by solvent molecules which hinders their escape into space and facilitates the reverse reaction. The latter has been called geminate recombination. The proposed explanation has been confirmed by numerous experiments, in particular by the decrease of the quantum yield of the dissociation of molecules with increase of the viscosity of the medium.[1] According to modern terminology, the "cage effect" involves the recombination of geminate pairs in competition with the escape of radicals into space.

The "cage effect" has been studied experimentally by the photolysis or thermolysis in the liquid phase of compounds which readily decompose into radicals (peroxides, azo-compounds, etc.). The reaction is carried out in the presence of effective radical acceptors. The radicals which have escaped into space react with the acceptor to form a product other than the products of the reaction of the radicals in the cage. Thus, in the photolysis of azoethane in n-heptane in the presence of large amounts of styrene, some of the ethyl radicals formed emerge from the cage and add to styrene. In the cage the ethyl radicals either combined to form butane or disproportionate to form ethylene and ethane. The ratio $(C_4H_{10} + C_2H_4)/N_2$ represents the fraction of radicals which have reacted in the cage. This quantity increases from 46 to 84% with decrease of temperature from +99° to −75 °C. The decrease of temperature increases the viscosity of the medium, which hinders the emergence of the radicals from the cage. The photolysis and thermolysis of many compounds in various solvents have been studied at different temperatures and viscosities of the medium; the dimensions of the radicals formed have also been varied.[10,11]

The "cage effect" also determines the effectiveness of initiators of chain radical processes. The effectiveness of the initiators of the polymerisation of vinyl monomers, which determines the fraction of the radicals emerging into space on decomposition of the initiator, has been studied in particular detail. Thus the effectiveness of initiation by azobisisobutyronitrile is 0.5–0.7, while for benzoyl peroxide it amounts to 0.7–1.0.[12]

Numerous experiments have shown that even active radical acceptors, reacting with all the radicals which have emerged into space, cannot compete with the recombination in the cage. The decomposition of azobisisobutyronitrile in liquid bromine may be an exception; in this case products of the recombination in the cage were not detected.[13] It is not clear whether it is possible to reach an unambiguous conclusion from this not altogether usual experiment.

A quantitative theory of the "cage effect" was formulated on the basis of the diffusion gradient method[5] and also the Noyes' method of molecular pairs.[1] Both methods yield identical expressions for the "cage effect" but use different parameters. We shall consider the diffusion gradient method, which makes it possible to formulate the problem exactly. Suppose that the distance between the radicals at the instant of the generation of the pair is l. Under the conditions of the experiments examined above, there is continuous generation and destruction of the radical pairs. As a result of this, after a time of the order of R^2/D (much shorter than the duration of the experiment), a stationary concentration of the pairs is established in the system. According to the

clear model of the diffusion gradient method which we adopted, point particles are continuously generated on the surface of a sphere with a radius l and diffuse "outwards" (dissociation of the pair) and "inwards", where they are destroyed with a certain probability on the inner surface of a sphere with a radius R (geminate recombination). The fraction of the recombination ϕ is determined by the ratio of the diffusion fluxes:

$$\varphi = \frac{4\pi R^2 D \left| \frac{\overleftarrow{dc}}{dx} \right|_R}{4\pi l^2 D \left(\left| \frac{\overleftarrow{dc}}{dx} \right|_l + \left| \frac{\overrightarrow{dc}}{dx} \right|_l \right)} , \qquad (19)$$

where c is the concentration of the point particles and the arrows $\leftarrow$ and $\rightarrow$ indicate the directions of the diffusion fluxes "within" and "outside" a sphere with a radius l. The concentration gradients in Eqn.(19) are found by solving the stationary diffusion equation for the case of spherical symmetry with allowance for the reaction of the radicals with the acceptor¶:

$$\frac{D}{x} \frac{d^2(cx)}{dx^2} - k_a c[\mathrm{Ac}] = 0 , \qquad (20)$$

where [Ac] is the acceptor concentration and k_a the rate constant for the reaction of the acceptor with the radicals; the boundary conditions are $x \to \infty$, $c \to 0$; $x = R$, $c = c_0$. The rate of recombination is determined by the diffusion flux through a surface $4\pi R^2$. The rate of recombination can also be represented in the form $k_2 c_0$ (see above). We thus obtain the expression

$$\Phi = 4\pi R^2 D \left| \frac{dc}{dx} \right|_R = k_2 c_0 . \qquad (21)$$

This equation makes it possible to eliminate the unknown quantity c_0. As a result, we obtain the following expression for ϕ:

$$\varphi = \frac{R \exp[-b(l-R)]}{l[1 + 4\pi RD(1 + bR)/k_2]} , \qquad (22)$$

where

$$b \equiv (k_a[\mathrm{Ac}]/D)^{1/2} .$$

In the first place it is necessary to estimate bR. The rate constant for the addition of the reactive radical such as the methyl radical or the polymeric vinyl acetate radical to a typical radical acceptor (styrene) at 60 °C is of the order of 10^5 litre mol^{-1} s^{-1} [12] or 0.17×10^{-15} cm^3 s^{-1}. For the usual values $D = 2 \times 10^{-5}$ cm^2 s^{-1} and $R = 5 \times 10^{-8}$ cm and for [Ac] = 10 M, we obtain k_a[Ac] = 10^6 s^{-1} and $bR \leq 0.01$. Then Eqn.(22) becomes

$$\varphi = \frac{R}{l} \frac{k_2}{k_2 + 4\pi RD} . \qquad (23)$$

It was found that the quantum yield γ of the photodissociation of iodine decreases with increase of the wavelength of light from 0.83 at $\lambda = 4047$ Å to 0.11 at $\lambda = 7350$ Å.[14] This dependence can be explained by the fact that, with decreased energy of the quantum, the kinetic energy of the translational movement of the iodine atoms moving apart, given by $h\nu - E_{\mathrm{diss}}$, diminishes, which leads to a decrease of l and hence of γ, since $\gamma = 1 - \phi$. This type of dependence has not been observed in he photodissociation of azo-compounds, which leads to the formation of the CH_3 or CF_3 radicals.[15] Evidently in these cases the $h\nu - E_{\mathrm{diss}}$ excess energy is converted into the vibrational energy of the radicals formed and does not lead to their separation, i.e. contact or "almost" contact pairs arise. The results of a study[16] in which it was shown that the "cage effects" are the same in the thermolysis and photolysis of azo-compounds also agree with this conclusion. Since the radicals formed on thermolysis do not possess an excess translational kinetic energy, it is evident that the photolysis also does not lead to the separation of the radicals.

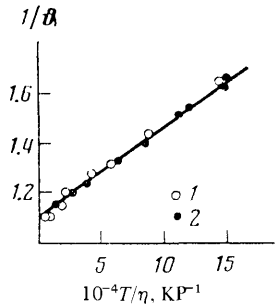


Figure 1. Dependence of $1/\phi$ on T/η; ϕ is the probability of the formation of C_2H_6—the product of geminate recombination in the photodecomposition of azomethane at temperatures from +98° to −72 °C: 1) ethyl acetate; 2) hexane.[5]

If RD is expressed in terms of T/η in accordance with the Stokes–Einstein formula, we obtain from Eqn.(23)

$$\frac{1}{\varphi} = \frac{l}{R} + \frac{l}{R} \frac{8kT}{3k_2 f\eta} . \qquad (24)$$

Figs.1 and 2 present the dependence of $1/\phi$ on T/η according to Eqn.(24) (see also Dobis et al.[15] and Chakravorty et al.[18]). A number of conclusions can be drawn from these data.

1. The ratio $l/R \cong 1$ when the radicals are formed simultaneously with ejection of the N_2 molecule (for example, in the photolysis of CH_3–N=N–CH_3) or $l/R \cong 2$ when the formation of the radicals is accompanied by the ejection of two CO_2 molecules [for example, in the photolysis of

$$(CH_3)_3COOC{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}OO(CH_3)_3 .$$

Evidently a contact radical pair is formed in the former case, which agrees with the considerations expressed above, while in the latter case one CO_2 molecule separates the $(CH_3)_3CO$ radicals at the instant of formation of the pair, so that $l/R \cong 2$.

2. The slope of the linear $1/\phi - T/\eta$ plots makes it possible to calculate the quantity $k_2 f$. This feature requires a more detailed discussion. The geminate recombination of the $\dot{C}H_3$ and $\dot{C}F_3$ radical depends little on the nature of the solvent and ϕ is determined solely by the quantity T/η, while the recombination of t-butoxy-radicals exhibits a definite dependence on the solvent.[17] The straight line in Fig.2 corresponds to aliphatic solvents. For olefins and aromatic solvents with the same fluidities of the medium, the quantities $1/\phi$ are much greater, which indicates smaller values of the

¶ In Denisov's review,[10] this method of analysis of the "cage effect" has been erroneously called the method of "one-dimensional translational diffusion".

constant k_2. For alcohols, the values of k_2 are even smaller, since only traces of geminate recombination products have been detected in such media. The deviation from the straight line must be explained by the specific interaction of the butoxy-radicals with the solvents indicated, which hinders the recombination and facilitates the emergence of the radical into space.[17]

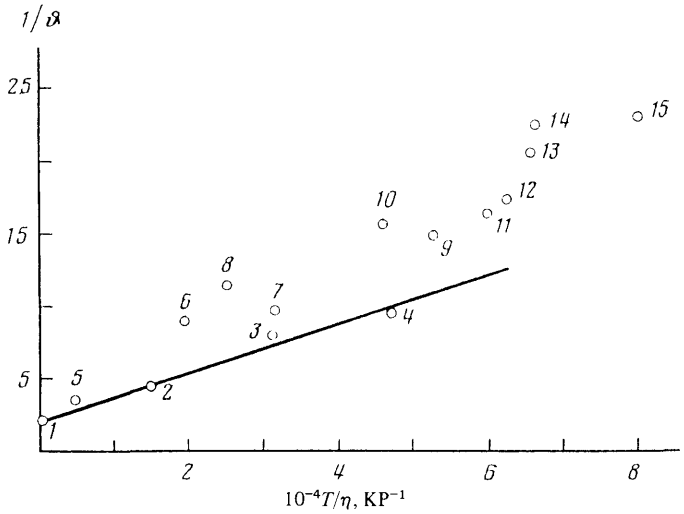


Figure 2. Dependence of $1/\phi$ on T/η; ϕ is the probability of the geminate recombination of t-butoxy radicals in various media: 1) liquid paraffin; 2) hexadecane; 3) dodecane; 4) decane; 5) dimethyl phthalate; 6) tetralin; 7) *o*-dichlorobenzene; 8) acetophenone; 9) cumene; 10) α-methylstyrene; 11) ethylbenzene; 12) cyclohexane; 13) toluene; 14) benzene; 15) oct-1-ene. The plot has been constructed on the basis of the data of Niki and Kamiya.[17]

Table 1. Kinetic constants for the recombination of radicals.

Constant, litre mol^{-1}s^{-1}	$\dot{C}H_3 + \dot{C}H_3$	$\dot{C}F_3 + \dot{C}F_3$	$(CH_3)_3\dot{C}O + O\dot{C}(CH_3)_3$
$10^{-10}\,k_2$	6.0 [5]; 11.7 [15]	1.4 [18]	0.41 [17]
$10^{-10}\,k^{gas}$	2.0 [19]	2.3 [19]	0.43±0.05 [20]
$10^{-10}\,Z^{gas}$	8.2	6.8	6.6

The constants k_2, determined from the slopes of the plots of $1/\phi$ against T/η (the multiplier f was assumed to be 0.65), are compared in Table 1 with the experimental recombination constants for the same radicals in the gas phase k_{gas} and with the calculated number of collisions Z in gases. The recombination constants in the gas phase for the methyl and trifluoromethyl radicals are ~1/4 of the number of collisions. This ratio corresponds to the probability that the spins of the colliding radicals are antiparallel. The recombination constant for the butoxy-radicals in the gas phase is much smaller than the number of collisions. For the methyl and butoxy-radicals, the rate constant k_2 is greater by a factor of 3–4 than the recombination constant in the gas phase. This can be explained by the fact that the geminate pair of radicals formed on photolysis is in a singlet state.[5] A difference between the constants has not been observed for the trifluoromethyl radical. However, one should treat all these conclusions with caution bearing in mind the experimental accuracy. There is only one reliable conclusion: the constants k_2 differ from the recombination constants in gases k_{gas} by a factor not greater than 2–3.

If a contact radical pair is formed, i.e. $R = l$, then the probability of recombination can be represented by Eqn.(17):

$$\varphi = k_1/(k_1 + k_d). \qquad (17)$$

Since the lifetime of the radical pair formed on photolysis or thermolysis is of the order of R^2/D, presumably a nonstationary value corresponding to Eqn.(6) must be adopted for k_d. If, however, the duration of the photolysis (thermolysis) greatly exceeds the lifetime of the pair, then a stationary value of D/R^2 enters into Eqn.(17). This can be demonstrated by the following calculation. Suppose that the pairs are formed at a rate I, whereupon $I\mathrm{d}\tau$ pairs are formed during the period $\mathrm{d}\tau$. The number of recombined pairs $\Delta(RR)$ during time t is defined by the expression

$$\Delta(RR) = k_1 I \int_0^t \left\{k_1 + \frac{D}{R^2}\left[1 + \left(\frac{R^2}{\pi D(t-\tau)}\right)^{1/2}\right]\right\}^{-1} \mathrm{d}\tau\,, \qquad (25)$$

After integration, it can be shown that, for $t \gg R^2/D$, the fraction of the recombined pairs is given by the expression

$$\varphi = \frac{\Delta(RR)}{It} = \frac{k_1}{k_1 + D/R^2}\,. \qquad (26)$$

In pulsed laser photolysis, where $t_{pulse} \cong R^2/D$, a nonstationary expression must be used for k_d (see below).

If the existence of very effective radical acceptors, for which $k_a[\mathrm{Ac}] > 10^6\ \mathrm{s}^{-1}$ is assumed, then there is a possibility of competition between the acceptors and geminate recombination. Having put $l = R$, Eqn.(22) can be expressed in the form

$$\varphi = \frac{\varphi_0}{1 + (1-\varphi_0)(k_a[\mathrm{Ac}]R^2/D)^{1/2}} \simeq \varphi_0\{1 - (1-\varphi_0)(k_a[\mathrm{Ac}]R^2/D)^{1/2}\}\,, \qquad (27)$$

where

$$\varphi_0 = k_2/(k_2 + 4\pi RD) = k_1/(k_1 + D/R^2)$$

is the fraction of geminate recombination in the absence of radical acceptors. It follows from Eqn.(27) that, in the presence of effective acceptors, ϕ should diminish as a linear function of $[\mathrm{Ac}]^{1/2}$. The influence of acceptors on recombination in the cage has also been represented in other forms,[1,21] but the linear dependence of ϕ on $[\mathrm{Ac}]^{1/2}$ remains.

4. Kinetics of the Recombination of Geminate Radical Pairs

The kinetics of geminate recombination can be investigated only by pulse methods. In the first study of this type,[22] the dissociation of the iodine molecule into atoms and their subsequent recombination in hexadecane and in carbon tetrachloride were followed by the method of picosecond photolysis. After 300–500 ps, geminate recombination reaches completion and an appreciable fraction of the iodine atoms emerge into space. An analogous study has been carried out in liquid xenon.[23] The kinetics of the geminate recombination in these studies have been discussed on the basis of the Noyes method of molecular pairs.[1] In this procedure use is made of the function $h(t)$, which expresses the probability that, after the first encounter between the molecules (radicals), a

second encounter takes place at a time between t and $t + dt$. Noyes proposed an approximate expression for the function $h(t)$:

$$[h(t) = pt^{-3/2}e^{-qt}] \quad , \qquad (28)$$

where p and q are constants. In this case the first encounter involves the formation of the geminate pair and the second encounter leads to reaction with a certain degree of probability. [The exact expression for the function $h(t)$ obtained by the diffusion gradient method[2] differs greatly from Eqn.(28).] Only an approximate agreement between Eqn.(28) and experiment has been noted.[22] In another study the[23] agreement with experiment was achieved by selecting three parameters. There is reason to believe that the picosecond dissociation of I_2 is complicated by phenomena which have no bearing on the geminate recombination.[24]

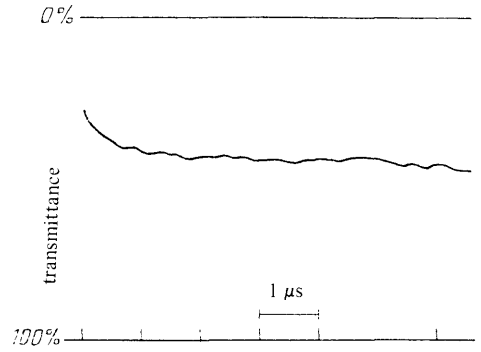


Figure 3. Kinetics of the geminate recombination of indandionyl radicals in liquid paraffin at 0 °C; T/η = 40 K P^{-1}.[26] For explanation, see text.

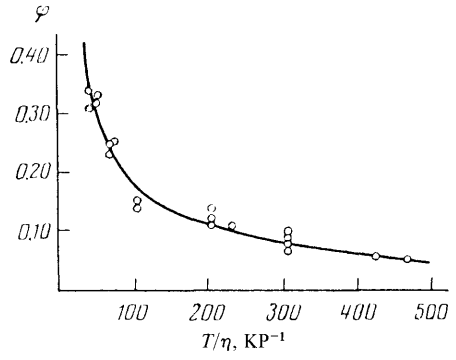
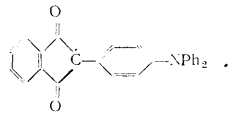


Figure 4. The fraction of the geminate recombination ϕ of indandionyl radicals as a function of the fluidity of the medium.[25]

The kinetics of the geminate recombination of indandionyl radicals, arising in the nanosecond photolysis of the corresponding dimer, have been studied:[25,26]



The geminate recombination has been observed only in viscous media (mixtures of hexane with liquid paraffin) in the region of fluidities below 500 K P^{-1}. Fig.3 illustrates typical kinetics of geminate recombination. The initial passage of the probing beam is determined by radical pairs and the plateau is due to the radicals which have escaped into space. Fig.4 shows the dependence of the fraction of geminate recombination ϕ on T/η. Analysis of the data on the "cage effect" leads to the conclusion that contact (or "almost" contact) radical pairs are formed on photolysis and thermolysis even in a mobile medium. Only on photodissociation of I_2 do I atoms move apart to distances exceeding the sum of their radii.[14]

We shall consider the kinetics of the geminate recombination of the contact radical pairs in terms of the "approximation of chemical kinetics".[6,26,27] The essential feature of this approximation consists in the fact that the rate of destruction of the given species is formulated in terms of the kinetic equations of homogeneous chemical kinetics, i.e. as the sum of the rates of formation and destruction of the given species via different pathways, including both chemical and diffusion processes. The rate constant for diffusion process, which in the general case depend on time, is found by solving the corresponding diffusion equation for point particles. For example, the rate constants for the formation and dissociation of pairs are determined by Eqns.(4) and (6). In terms of this approximation, the destruction of the contact radical pairs, which have arisen after the completion of the pulse, is determined by the equation

$$-\frac{dn}{dt} = k_1 n + \frac{D}{R^2}[1 + R(\pi D t)^{-1/2}]n \, . \qquad (29)$$

The first term represents the destruction of the pairs as a result of geminate recombination and the second as a result of the dissociation of the pairs [see Eqn.(6)]. The integration of Eqn.(29) yields

$$\frac{n}{n_0} = \exp\{-[(1 + a^2)k_1 t + 2a(\pi k_1 t)^{1/2}]\} \, , \qquad (30)$$

where $a^2 = D/R^2 k_1$ is the ratio of the stationary rate constant for the dissociation of the pair to the geminate recombination constant and n_0 is the initial concentration of the pairs. The fraction of pairs which have recombined during time t is

$$\varphi(t) = k_1 \int_0^t \frac{n}{n_0} dt = [1 - \exp(A^2 - z^2) - \sqrt{\pi} A \, e^{A^2}(\mathrm{erf}\, z - \mathrm{erf}\, A)]/(1 + a^2), \qquad (31)$$

where

$$A = a/[\pi(1 + a^2)]^{1/2} \text{ and } z = A + [(1 + a^2)k_1 t]^{1/2}.$$

When $t \to \infty$, Eqn.(31) becomes

$$\varphi = [1 - \sqrt{\pi} A \, e^{A^2} \mathrm{erfc}\, A]/(1 + a^2) \, . \qquad (32)$$

Eqn.(32) represents the fraction of recombined radical pairs under the conditions of non-stationary recombination kinetics. In terms of the approximation of chemical kinetics, this quantity is smaller than the fraction of the recombined radical pairs under stationary conditions, which is $(1 + a^2)^{-1}$.

5. The Multiplicity of the Radical Pair

For a more rigorous description of the kinetics of the recombination of a radical pair, it is necessary to take account of its multiplicity. The radical pair can exist in two extreme states: singlet or triplet. It follows from the quantum theory that the multiplicity of the pair varies continuously through a sequence of mixed states (see, for example, Buchachenko[28]). This phenomenon has come to be called spin evolution. The probability of the recombination of the radical pair is higher the greater the contribution of the singlet state to the multiplicity of the pair. The radical pair existing in a purely triplet state cannot recombine.

There are various mechanisms of the changes in the multiplicity of the radical pair. The following are of real importance.

1. The Δg-mechanism. This mechanism is manifested following the imposition of an external magnetic field. According to this mechanism, the rate of spin evolution is determined by the difference between the magnetic energies of the unpaired electrons of the radical pair. The energy of an electron in a magnetic field H is $\frac{1}{2}g\beta H$, where β is the Bohr magneton (0.927×10^{-20} erg G^{-1}) and g a proportionality coefficient—the so-called g-factor, which is determined from the EPR spectrum. For a free electron, $g = 2.0023$; for the unpaired electron in the radical, the g-factor differs from this value as a consequence of the spin–orbital coupling and depends on the type of the radical. In a magnetic field the triplet state of the radical pair is split into three sublevels T_-, T_0, and T_+, among which only the energy of the T_0 sublevel coincides with that of the pair in a singlet state (subject to the condition that there is no exchange interaction in the pair). Only T_0–S transitions, whose probability vary with time as $\sin^2(\frac{1}{2}\Delta g\beta Ht/h)$,[29] where $h = h/2\pi$ (h is the Planck constant), therefore occur in a magnetic field. In this expression

$$\left(\frac{1}{2}\right)\Delta g\beta H/\hbar = \left(\frac{1}{2}\right)2\pi\Delta g\beta H/h$$

represents the difference between the magnetic energies of the unpaired electrons expressed in units of rad s^{-1}. [This unit of measurement of the energy is obtained by dividing the magnetic energy of the electron $\frac{1}{2}g\beta H$ (ergs) by h (erg s), which yields the energy in s^{-1}, and by multiplying by 2π, which yields the energy in units of rad s^{-1}.]

If in the initial instant the pair exists in a purely singlet state, then after a time t_S, whereupon $\frac{1}{2}2\pi\Delta g\beta Ht_S/h = \pi/2$, the pair passes to a purely triplet state. The quantity $k_S = 1/t_S$ can be adopted, with some approximation, as the constant of the T_0–S transition, i.e. $k_S = 2\Delta g\beta H/h$. Since the quantities Δg are usually in the range 10^{-2}–10^{-3}, it follows that we obtain $k_S = 2.8 \times 10^8$–2.8×10^7 s^{-1} for $H = 10^4$ G.

2. The HFI-mechanism. Another mechanism leading to spin evolution is a consequence of the magnetic interaction of the unpaired electron with paramagnetic nuclei (usually with protons, but also with ^{13}C, ^{17}O, ^{19}F, ^{31}P, etc. nuclei). Since this interaction leads to splitting of the EPR line into a series of components, i.e. to a hyperfine structure of the spectrum, it has come to be called the hyperfine interaction (HFI). Quantitatively the HFI interaction is characterised by an HFI constant, which is determined from the EPR spectrum and is usually expressed in gauss. The HFI-mechanism of spin evolution also depends on the external magnetic field, but this dependence is of a type different from that in the case of the Δg-mechanism. In the absence of the magnetic field, all three sublevels of the triplet state of the pair are degenerate and their energies coincide with the energy of the singlet state. Under these conditions, the transition from the singlet state is to all three sublevels of the triplet state. When an external magnetic field is imposed, only the T_0–S transition takes place as a consequence of the splitting of the triplet level, which usually leads to a decrease of the probability of the transition. We may note that the necessary splitting of the triplet level is achieved in magnetic fields amounting to several tens or hundreds of gauss.

A quantitative analysis of the HFI-mechanism is difficult, particularly because the radical pair usually contains several paramagnetic nuclei, for example, protons, which are in the general case characterised by different HFI constants and this leads to a complex picture of spin evolution. Expressions have been published[29] for the probabilities of the S–T transitions for certain simple model radical pairs. For example, for the radical pair

$$\dot{R}^1 \cdots \dot{R}^2 \begin{matrix} \nearrow H \\ \searrow H \end{matrix}$$

in the absence of an external field, the probability of the S–T transition varies with time as $^2/_3 \sin^2(^3/_4At)$. The parameter A (rad s^{-1}) is related to the HFI energy, equal to $a\beta$, by the expression $A = 2\pi a\beta/h$, where a is the HFI constant (G) and β the Bohr magneton (erg G^{-1}). As in the case of the Δg-mechanism, for the time t_S corresponding to a change in the multiplicity of the pair we shall adopt the condition $^3/_4At_S = \pi/2$, whence it follows that $1/t_S = k_S = 3a\beta/h$. If $a = 100$ G, then $k_S = 0.4 \times 10^9$ s^{-1}. For other radical pairs, one should expect values of k_S of the same order of magnitude for the same values of a. If one radical contains m protons and the other n protons, then the extent of the HFI in the pair can be approximately calculated with a single effective HFI constant a_{eff}, which is defined by the formula

$$a_{eff} = \left(\sum_m a_m^2 + \sum_n a_n^2\right)^{1/2} . \qquad (33)$$

The periodic evolution of the spin state of the pair was observed experimentally for the first time by Anisimov et al.[30] A solution of tetramethylethylene (D) and perdeutero-*p*-terphenyl (A) in a non-polar solvent proved to be a convenient object for investigation. The ionisation of the solvent under the influence of ^{90}Sr radiation generates pairs of radical-ions ($D^+.A^-$) as a result of electron capture by the molecule of A and electron transfer from D to the solvent radical-cation. In the radical-ion D^+ all the protons are equivalent, while the HFI constants for A^- are small. In this case the picture of spin evolution simplifies and can be observed from the periodic maxima of the recombination fluorescence arising on recombination of the pair (electron transfer from A^- to D^+) with formation of a fluorescent molecule A*. These maxima are observed particularly clearly following the imposition of a magnetic field (3300 G), which leads to a further simplification of the picture of spin evolution as a consequence of the "disconnection" of the T_+ and T_- states. The recombination fluorescence maxima continued in succession over a period of 22 ns, which corresponded, according to a theoretical calculation,[31] to the maximum in the contribution of the singlet state of the pair.

An important feature of the HFI-mechanism is that a change in the multiplicity of the radical pair is accompanied by selection with respect to the orientations or reorientations of the spins of the paramagnetic nuclei. Since the relaxation of the nuclear spins is slow (minutes), the ratio of the molecules with the orientation of the nuclear spin along the magnetic field and in opposition to the field in the radical pair recombination products differs from the Boltzmann ratio. This phenomenon, which has come to be called chemically induced nuclear polarisation, has been described in detail in

a monograph[28] and in a review.[32] The phenomenon of chemically induced radioemission is also associated with the polarisation of nuclear spins on recombination of radical pairs.[33] If the radical pair contains a paramagnetic isotope, for example ^{13}C, then, as a consequence of the influence of the paramagnetic nucleus on the spin evolution, certain recombination products are enriched in the paramagnetic isotope—the magnetic isotope effect.[32,34,35] For all these phenomena, the observed effect is determined by competing processes involving spin evolution, recombination, and diffusion separation of the pair. The discussion of these interesting phenomena is outside the framework of the present review.

It is also necessary to consider the influence of the exchange interaction of unpaired electrons on the spin evolution. If this interaction is intense, then the spin evolution is hindered as a consequence of the appearance of an energy difference between the T_0 and S states. It is usually assumed, following the Noyes theory, that the radicals of the pair execute a series of repeating encounters as a consequence of molecular movement. In the intervals between these encounters the exchange energy is small and spin evolution reaches completion. However, spin evolution can be completed also in contact (or "almost" contact) pairs. As a result of the diffusional rotation of the radicals of the pair, the wave functions of the unpaired electrons do not overlap for a considerable proportion of the lifetime of the pair and the exchange interaction is therefore weak. The characteristic time of rotational diffusion is of the same order of magnitude as the characteristic time of translational diffusion[36] and spin evolution can therefore compete with the diffusional separation in the pair and also with the recombination of the radicals of the pair.

6. The Probability of the Recombination of the Radical Pair taking into account Spin Evolution

Theoretical consideration of the recombination of radical pairs taking into account spin evolution and the influence of the magnetic field is a complex task. It was shown in the previous Section that spin evolution can be approximately characterised as unimolecular $T-S$ transitions. In terms of the approximation of the methods of chemical kinetics, the behaviour of the radical pairs can then be described by the following scheme of elementary processes,[26] different variants of which have been used in many experimental studies:

$$\begin{array}{ccc} R{-}R & \underset{k_1}{\overset{}{\leftarrow}} & {}^1(R\cdot R) \underset{k_S}{\overset{3k_S}{\rightleftarrows}} {}^3(R\cdot R) \\ & & \downarrow k_d \qquad \downarrow k_d \\ & & R + R \qquad R + R \end{array} .$$

We shall carry out a kinetic analysis of this scheme.[26] The rate constant for the transition from the triplet to the singlet state is designated by k_S, whereupon the rate constant for the reverse transition (in the absence of a magnetic field) is $3k_S$ as a consequence of the triple degeneracy of the triplet state of the pair. Suppose that at a certain instant there are [P] pairs, among which there are [S] singlet pairs and [T] triplet pairs. The fraction of pairs which have recombined during time t is

$$\varphi(t) = \frac{k_1}{[P]} \int_0^t [S]\, dt \quad . \qquad (34)$$

The concentration of the singlet pairs can be found in terms of the approximation of chemical kientics by solving a system of kinetic equations for the singlet and triplet pairs:

$$\frac{d[S]}{dt} = k_S[T] - k_1[S] - k_d[S] - 3k_S[S] \; ; \qquad (35)$$

$$\frac{d[T]}{dt} = -k_S[T] - k_d[T] + 3k_S[S] \; . \qquad (36)$$

In the general case the constant k_d depends on time in accordance with Eqn.(6). We shall consider the application of Eqns.(34)–(36) in the description of geminate and volume recombination.

Geminate recombination. Geminate pairs arise either in the singlet or triplet state depending on the spin state of the initial molecule at the instant of dissociation. In the general case the characteristic time of geminate recombination is of the same order of magnitude as the lifetime of the pair. Consequently the following non-stationary quantity must be adopted for k_d:

$$k_d = \frac{D}{R^2}\left[1 + R(\pi D t)^{-1/2}\right] .$$

We shall consider special cases.

(a) The pairs arise in the triplet state and the time of transition to the singlet state is much greater than the dissociation time of the pair, i.e. $k_d \gg k_S$. In this case geminate recombination does not occur and all the pairs dissociate.

(b) The pairs arise in the triplet state, the transition to the singlet state is slow, and the recombination in the singlet state is rapid, i.e. $k_1 \gg k_S$. The rate of recombination is then determined by the rate of the process $T \to S$, which is equal to $k_S[T]$. Since in this case $[T] \gg [S]$, then neglecting the term $3k_S[S]$ in Eqn.(36), we arrive at Eqns.(29) and (32), in which k_S replaces k_1, i.e. the probability of the recombination is determined by the rate of transition of the pair to the singlet state in competition with the diffusional separation of the pair.

(c) The pairs arise in the singlet state and the transition to the triplet state is slow, i.e. $k_d \gg k_S$. The first two terms of Eqn.(35) can then be rejected, leading to Eqns.(29) and (32). In this case the probability of recombination is independent of the rate of spin evolution.

(d) If the spin evolution is very rapid, i.e. $k_S \gg k_d$ and $k_S \gg k_1$, then, regardless of the initial spin state of the pair, a spin equilibrium is established in which $[T] = 3[S]$. Having added together Eqns.(35) and (36), we again arrive at Eqn.(29), in which $k_1/4$ replaces k_1. This special case obtains in a viscous medium at a very high rate of spin evolution.

Thus, for all the special cases considered, the kinetics of the geminate recombination are described by Eqn.(29) and we obtain Eqn.(32) for the probability of recombination, in which the constant k_1 is modified for different special cases, as shown above.

In order to obtain a general expression for the kinetics of geminate recombination, it is necessary to solve Eqns.(35) and (36). An approximate solution can be obtained if the average value of k_d during the lifetime of the pair τ is adopted:

$$\bar{k}_d = \frac{D}{R^2\tau}\int_0^\tau \left[1 + R(\pi D t)^{-1/2}\right] dt \simeq 2.13D/R^2 \; . \qquad (37)$$

The coefficient 2.13 is obtained if one puts $\tau = R^2/D$. We then obtain for the probability of geminate recombination the same equations as for the volume recombination (see below), in which the average value $\bar{k}_d$ should be substituted for k_d.

Volume recombination. The geminate pairs which have dissociated with liberation of the radicals into space give rise to a volume concentration of radicals. The recombination takes place in space following the encounter of the radicals which have emerged from different pairs and produced secondary

pairs. Since the characteristic time of the volume recombination greatly exceeds the lifetime of the pair and the time of attainment of the stationary value of k_d, it follows that $k_d = D/R^2$ (see above). In this case Eqns.(35) and (36) are easily solved under specified initial conditions and expressions are obtained for [S] and [T] as functions of time. Integration of Eqn.(34) from 0 to ∞ yield expressions for ϕ for pairs arising in the singlet state:

$$\varphi_S = \frac{k_S k_1 + k_d k_1}{k_S k_1 + 4k_S k_d + k_1 k_d + k_d^2} \quad (38)$$

and for those arising in the triplet state:

$$\varphi_T = \frac{k_S k_1}{k_S k_1 + 4k_S k_d + k_1 k_d + k_d^2} \quad . \quad (39)$$

Since one-quarter of the pairs are formed in the singlet state and three-quarters are formed in the triplet state in an encounter between radicals in space, the overall probability of the recombination is defined by the expression

$$\varphi = \frac{1}{4}\varphi_S + \frac{3}{4}\varphi_T \quad (40)$$

or

$$\varphi = \frac{k_S k_1 + \frac{1}{4}k_1 k_d}{k_S k_1 + 4k_S k_d + k_1 k_d + k_d^2} \quad . \quad (41)$$

Certain special cases are of interest.

1. During the lifetime of the pair there is insufficient time for spin evolution, i.e. $k_d \gg k_S$. It then follows from Eqn.(41) that

$$\varphi = \frac{1}{4}k_1/(k_1 + k_d) \quad . \quad (42)$$

If in addition we have under these conditions $k_1 \gg k_d$, then $\phi = {}^1/_4$. In this case the bimolecular recombination constant $k_{exp} = 4\pi RD/4$. This case can obtain in a fluid medium and also for a low rate of spin evolution.

2. The spin transformation times are much shorter than the lifetime of the pair, i.e. $k_S \gg k_d$. We then have

$$\varphi = k_1/(k_1 + 4k_d). \quad (43)$$

If in addition $k_1 \gg k_d$, then $\phi = 1$ and $k_{exp} = 4\pi RD = k_{diff}$. This case can obtain in viscous media and for high rates of spin evolution.

It is seen from the above analysis that the expressions for the radical recombination rate constant in the form $k_{exp} = 4\pi RD/4$ or $k_{exp} = 4\pi RD$, which are frequently encountered in the literature, in reality obtain only in special cases, while Eqn.(41) and special cases of the latter [Eqns.(42) and (43)] correspond to more realistic conditions and constitute a generalisation of Eqn.(17) obtained without taking into account spin transformations.

7. Determination of the Kinetic Constants for Radical Pairs from Experimental Data

A method has been proposed[26] for the determination of the kinetic constants k_1 and k_S from experimental data for the kinetics of the volume and geminate recombination over a wide range of fluidities of the medium T/η.

Volume recombination. The probability of the recombination of the pair ϕ_{exp}, formed in an encounter between radicals, can be determined experimentally from the equality

$$\varphi_{exp} = \frac{k_{exp}}{4\pi RD} \quad , \quad (44)$$

where k_{exp} is the bimolecular recombination constant. Having expressed RD in terms of T/η by means of the Stokes–Einstein formula [Eqn.(10)], we obtain

$$\varphi_{exp} = \frac{3k_{exp}f\eta}{8kT} \quad . \quad (45)$$

We set ϕ_{exp} equal to the theoretical quantity ϕ (see above). It is then possible to determine from the experimental data the constants k_1 and k_S; for this purpose, it is necessary to measure k_{exp} over a wide range of fluidities of the medium. We shall explain the method for the determination of the kinetic constants in relation to the recombination of indandionyl radicals arising in the nanosecond photolysis of the corresponding dimer.[26] In the above study the bimolecular recombination constant k_{exp} was measured in mixtures of toluene and liquid paraffin over a wide range of fluidities of the medium—from 50500 to 41 K P^{-1}. In the region of low fluidities ϕ_{exp} reaches a constant value, which is evidently unity. It follows from this normalisation that $f = 0.65$. With increase of the fluidity of the medium to 500 K P^{-1}, all the singlet pairs recombine with a probability of unity; the rate of recombination of triplet pairs is determined by the rate of their conversion into singlet pairs in competition with the dissociation of the pair. Consequently in this range of fluidities we have $k_1 \gg k_S$ and $k_1 \gg k_d$. It then follows from Eqns.(39) and (40) that

$$\varphi_{exp} = \frac{1}{4} + \frac{3}{4}\frac{k_S}{k_S + k_d} \quad , \quad (46)$$

where $k_d = D/R^2$. Application of the Stokes–Einstein formula leads to the expression

$$(1 - \varphi_{exp})/(\varphi_{exp} - 0.25) = \frac{4kT}{6\pi f\eta R^3 k_S} \quad . \quad (47)$$

A plot of $(1 - \phi_{exp})/(\phi_{exp} - 0.25)$ against T/η is presented in Fig.5. $R^3k_S = 0.3 \times 10^{-13}$ cm^3 s^{-1} can be obtained from the slope of the straight line†. For a fluidity of the medium in excess of 3000 K P^{-1}, the experimental points deviate from the straight line. Consequently in this range of values of T/η not all the singlet pairs recombine and some of them dissociate.

In the region of high fluidities of the medium, it has been found that $\phi_{exp} < 0.25$. Evidently under these conditions not only all the triplet pairs but also some of the singlet pairs dissociate. Consequently $\phi_T = 0$ and $k_d \gg k_S$ for the singlet pairs, while k_1 and k_d are of the same order of magnitude. For this range of values of T/η, it follows from Eqns.(38) and (40) that

$$\varphi_{exp} = \frac{1}{4}k_1/(k_1 + k_d) \quad . \quad (48)$$

Having set Eqns.(45) and (48) equal to each other, we obtain

$$\frac{1}{k_{exp}} = \frac{3f\eta}{2kT} + \frac{1}{\pi R^3 k_1} \quad . \quad (49)$$

Fig.6 illustrates the dependence of $1/k_{exp}$ on η/T in the region of high fluidities and it follows from the plot that $f = 0.33$ and $R^3k_1 = 9.1 \times 10^{-13}$ cm^3 s^{-1}. The absolute values of the constant k_1 and k_S can be determined if reasonable

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†The quantity $\bar{k}_d = 2.13\ D/R^2$ has been used.[26] As shown above, $k_d = D/R^2$ should be employed for the volume recombination. The constants k_1 and k_S quoted by Bagdasar'yan and co-workers[26,37] should be reduced by a factor of 2.13.

values are assumed for R. The study of the kinetics of the geminate recombination makes it possible to determine R directly from the experimental data (see below). Thus the following values of the constants have been obtained:

$$R=14.5 \text{ Å}, \ k_1=2.7\cdot10^8 \text{ s}^{-1}, \ k_S=9.0\cdot10^6 \text{ s}^{-1}.$$

For these values of the kinetic constants, Table 2 lists the recombination probabilities for singlet and triplet pairs calculated by Eqns.(38) and (39) and also the overall probability of recombination in the encounters between radicals in accordance with Eqn.(40).

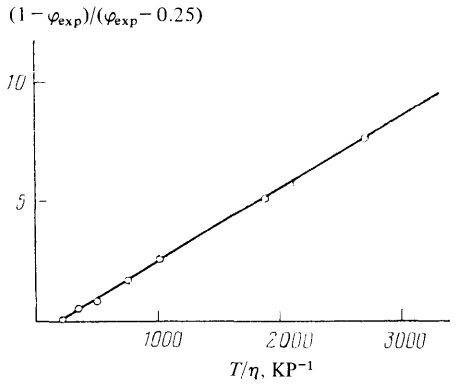


Figure 5. Dependence of $(1-\phi_{exp})/(\phi_{exp}-0.25)$ on T/η according to Eqn.(47) in the region of low fluidities.[26]

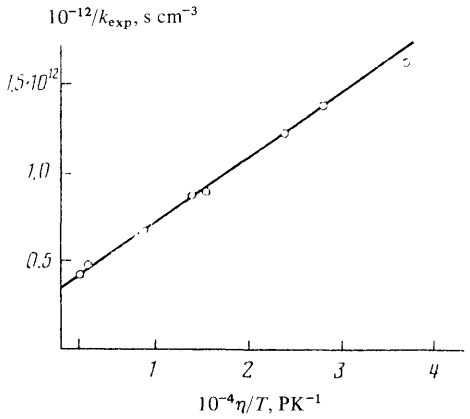


Figure 6. Dependence of $1/k_{exp}$ on η/T according to Eqn.(49) in the region of high fluidities.[26]

Geminate recombination. The kinetics of the geminate recombination of the indandionyl radicals, which have been observed only in a viscous medium (see Fig.4), obey Eqn.(31).[26] In this equation k_1 should be replaced by the constant k^*, which can have the significance of k_1^* or k_S^* depending on the state in which the geminate pair was generated: singlet or triplet (the asterisk denotes constants referring to the geminate pair). In the latter case the recombination takes place only after the conversion of the triplet pair into the singlet pair. Using Eqn.(32), $a^2=D/R^2k^*$ is found from experimental ϕ_{exp}, after which a value of k^* satisfying Eqn.(31) is selected. For this purpose, it is convenient to employ a programmable microcalculator. Since

$$a^2=D/R^2k^*=4kT/R^3k^*6\pi\eta,$$

the plot of a^2 against T/η makes it possible to determine R^3k^*. Thus $k^* = 0.9\times10^6$ s^{-1} and $R = 14.5$ Å were obtained for the indandionyl radicals. The value of R found makes it possible to determine the volume recombination constants k_1 and k_S, which were quoted above.

Table 2. Probability of recombination in the encounters of the indandionyl radicals forming pairs in the singlet and triplet states (according to the data of Bagdasar'yan et al.[26]) ($R = 14.5$ Å, $k_1 = 2.7\times10^8$ s^{-1}, $k_S = 9.0\times10^6$ s^{-1}).

T/η, K P^{-1}	D/R^2, s^{-1}	Recombination probabilities		
		Φ_S	Φ_T	Φ
5	$2.2\cdot10^5$	1	1	1
50	$2.2\cdot10^6$	0.96	0.79	0.83
500	$2.2\cdot10^7$	0.88	0.25	0.41
5000	$2.2\cdot10^8$	0.52	0.03	0.15
50000	$2.2\cdot10^9$	0.12	0	0.03

If the geminate pair arises in the singlet state, i.e. $k^* = k_1^* = 0.9\times10^6$ s^{-1}, then the constant k_1^* is 300 times smaller than k_1. If the geminate pair arises in the triplet state, then $k^* = k_S^*$ and the constant k_S^* is 10 times smaller than k_S. It may be that the cause of the difference between the constants is that the geminate pair has an excess energy of ~3 eV at the instant of formation and is in a highly vibrationally excited state, in contrast to the pair formed in the encounter between radicals.

The volume recombination of ketyl radical,[37] obtained by the photolysis of benzopinacone in mixtures of hexane with liquid paraffin having different fluidities (from 94400 to 410 K P^{-1}), has been investigated. Treatment of the experimental data by the method described above yielded the following constants: $k_S = 3\times10^8$ s^{-1} and $k_1 = 0.4\times10^{10}$ s^{-1}. In contrast to the indandionyl radicals, the geminate recombination of the ketyl radicals was not observed. Over the entire range of fluidities of the medium investigated, the pairs dissociate and the radicals are released into space. Evidently the pairs of ketyl radicals arise in the triplet state and their lifetime is not long enough for conversion into the singlet state. If the rate constants for the geminate and volume recombinations were identical, then geminate recombination might have been observed. Thus, as in the case of indandionyl radicals, the kinetic constants of the geminate and volume recombinations differ (or at least one of them is different).

8. The Influence of a Magnetic Field

Brocklehurst[38] was the first to put forward the idea that the influence of the magnetic field on the recombination of radicals is associated with the spin transformations in the radical pair. Later studies showed that the influence of the magnetic field is due to the Δg- and HFI-mechanisms of

the spin transformations. Certain examples of the influence of magnetic field on the recombination kinetics have been presented in reviews.[29,32] Systems for which the geminate pair constants have been determined and the influence of a magnetic field on the recombination of radicals has been observed will be considered below.

Under pulsed illumination (N_2 laser, duration of pulse 3 ns) of benzophenone (B) in solution in hexane, a hydrogen atom is transferred from hexane to a benzophenone molecule in the triplet state (^{3}B) with formation of a geminate pair in a triplet state consisting of the ketyl radical $\dot{B}H$ and the hexyl radical $\dot{R}$:[39]

$$^3B + RH \rightarrow {}^3(\dot{B}H\dot{R}) .$$

The second light pulse, emitted 38 ns after the first, induces the fluorescence of the ketyl radical. When a magnetic field whose strength is up to 8 kG is applied, the Δg interaction induces the $T_0 \rightarrow S$ transition and rapid recombination (reverse transfer of a hydrogen atom) of the singlet pair formed, which is accompanied by a decrease of the fluorescence intensity of the ketyl radical. If the HFI interaction were stronger than the Δg interaction, the opposite effect would have been obtained.

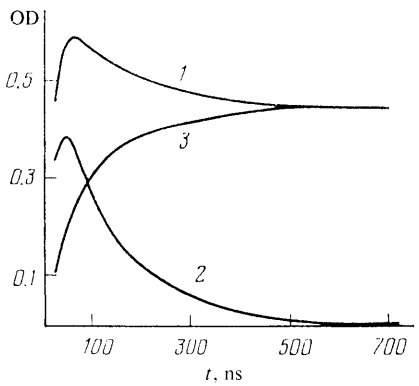


Figure 7. Kinetics of the variation of the optical density (OD) at 545 nm in the benzophenone–liquid paraffin system (η = 140 cP): 1) OD at λ = 545 nm; 2) ditto at λ = 620 nm multiplied by 3 (this is equal to the ratio $\varepsilon^{545}/\varepsilon^{620}$ for triplet benzophenone molecules); 3) difference between curves *1* and *2*.[40]

The analogous benzophenone–liquid paraffin system was investigated by nanosecond flash photolysis.[40] Fig.7 presents the kinetics of the variation of the optical density at λ = 545 nm (curve *1*) and λ = 620 nm (curve *2*) for η = 140 cP. The initial section of curve *1* is determined by the overall absorption by triplet benzophenone molecules and ketyl radicals, while the plateau on this curve corresponds to the absorption by ketyl radicals which have been released into space. Curve *2* corresponds to the absorption only by the triplet benzophenone molecules. It is seen that the triplets disappear at the instant when curve *1* reaches the plateau. Hence it follows that the destruction of the pairs $^3(\dot{B}H\dot{R})$ takes place immediately after their formation. Analysis of the experimental data leads to the conclusion that the ratio $k_d/(k_d + k_1) = 0.56$ and is independent of the viscosity of the medium. Consequently not only the dissociation of the pairs but also the transfer of a hydrogen atom from the ketyl radical to $\dot{R}$ depends on the viscosity of the medium. In the benzophenone–hexane system[39] the conversion of a triplet pair into a singlet pair competes with the dissociation of the pair. When hexane is replaced by liquid paraffin, the rate of dissociation of the pair diminishes by a factor of hundreds. Under these conditions, all the triplet pairs are converted into singlet pairs, which dissociate and recombine at approximately equal rates.

The $T-S$ transition can proceed also via the HFI-mechanism. In this case the application of a weak magnetic field decreases the probability of the $T-S$ transition as a consequence of the splitting of the triplet level and the disconnection of the T_+ and T_- states and hence decreases the fraction of the recombination process and increases the release of radicals into space. Studies of this type have been carried out in micellar solutions in which diffusional separation of the pairs is difficult, which favours spin transformations. Thus the nanosecond photolysis of various anthraquinones in a sodium dodecylsulphate solution has been studied.[41] A laser pulse results in the formation of the triplet radical pair $^3(Q\dot{R})$, where $\dot{R}$ is the radical formed from a solvent molecule and $\dot{Q}$ is a semiquinone radical. The application of a magnetic field up to 790 G slows down the destruction of the triplet pair and increases the release of the radicals into space. For anthraquinone, the constant k_S diminishes from 2.5×10^6 s^{-1} for $H = 0$ to 1×10^6 s^{-1} for H = 790 G; the constant k_d remains invariant at 1×10^6 s^{-1}.

The nanosecond photolysis of micellar solutions of benzophenone has been studied[42] in the presence of cyclohexadiene RH. A triplet pair $^3(\dot{B}H.\dot{R})$ arises under these conditions. The kinetics of the destruction of the triplet pair (it has been assumed that the destruction proceeds in accordance with a first-order reaction) and the fraction of the radicals released into space make it possible to determine the constants k_S and k_1. In a micellar solution of cetyltrimethylammonium bromide these constants are respectively 1.6×10^6 s^{-1} and 1.7×10^6 s^{-1}. The values obtained for sodium dodecylsulphate micelles are respectively 4.4×10^6 s^{-1} and 5.8×10^6 s^{-1}. When a magnetic field is applied, the release of radicals into space increases from 58% for $H = 0$ to 80% for H = 2000 G regardless of the nature of the micelles.

The spin effects and the influence of the magnetic field have been observed in the photoinitiation of emulsion polymerisation by triplet sensitisers.[43] For other methods of initiation of the emulsion polymerisation of the same monomers, the influence of a magnetic field has not been observed. The explanation is based on the considerations described above.

III. RADICAL-ION PAIRS

1. The Rehm–Weller Scheme

The behaviour of the radical-ion pairs arising as a result of the electron phototransfer will be considered in this section. The overall scheme of the phototransfer has been proposed by Rehm and Weller:[44]

$$A^* + D \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} (A \cdot D)^* \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} (A^{\cdot-} \cdot D^{\cdot+}) \begin{cases} \xrightarrow{k_d} A^{\cdot-} + D^{\cdot+} \\ \xrightarrow{k_1} A + D \end{cases} ,$$

where A* is an excited molecule of an electron acceptor, D an electron donor, (A.D)* an exciplex, i.e. an excited molecule with partial electron transfer or an excited unrelaxed acceptor–donor complex, and $(A^{\cdot-}.D^{\cdot+})$ a radical-ion pair

which can either recombine (reverse electron transfer) or can dissociate with formation of "free ions". The electron donor can also behave as an excited molecule. In order to complete this scheme, it is necessary to take into account the spin state of both the excited molecule and the radical-ion pair and also the possibility of the spin evolution of the pair. Thus in the phototransfer of an electron from dimethylaniline to an excited pyrene molecule in the singlet state, a radical-ion pair is produced in the excited singlet state, while the phototransfer of an electron with participation of a triplet benzophenone molecule leads to the formation of a pair in the triplet state. The energetic conditions necessary for the electron phototransfer and also the properties of the exciplexes have been examined in detail in a series of reviews and monographs[45,46] and will not be discussed in this paper. Here it is sufficient to note that, with increased dielectric constant of the medium ε, the lifetime of the exciplexes τ diminishes and there is a sharp increase of the rate constant k_e for the conversion of exciplexes into radical-ion pairs, as can be seen from Table 3.[47]

Table 3. Kinetic constants for the dimethylaniline–pyrene exciplex.[47]

Solvent	ε	τ, ns	$10^{-6}k_e$, s^{-1}
Acetonitrile	38	2.0	490
Methanol	33	9.4	95
Ethanol	24.5	19.8	41
Isopropyl alcohol	15.7	72.5	5
Tetrahydrofuran	4.6	102	~1
Diethyl ether	4.3	134.5	~1

On the basis of the Rehm–Weller scheme, we can obtain expressions for the phenomenological fluorescence quenching constant k_Q (or the constant for the destruction of the triplet state) and for the liberation of free ions. We shall assume that the process involving k_{32} can be neglected, i.e. that the vibrational relaxation is fairly rapid after the electron transfer (the process involving k_{23}). Under the conditions of steady-state illumination, stationary concentrations of the A*, (A.D)*, and ($A^{\bar{}}.D^{+}$) species are established in the solution. Having formulated the equations for the stationary state for the short-lived species indicated, in accordance with the above scheme, we arrive at the following expression for the quenching of the fluorescence (or the destruction of triplet states):

$$\frac{L_0}{L} = 1 + \frac{k_{12}\tau[D]}{1 + k_{21}/k_{23}} , \qquad (50)$$

where L_0 and L are the fluorescence intensities in the absence and presence of a quenching agent respectively and τ is the lifetime of the molecule A*. The empirical Stern–Volmer constant is expressed in terms of the constants for elementary processes in the following manner:

$$k_Q = \frac{k_{12}}{1 + k_{21}/k_{23}} . \qquad (51)$$

An expression for the quantum yield in the formation of free ions γ_{fi} can be obtained analogously:

$$\gamma_{fi} = \frac{\alpha_{fi}k_{12}\tau[D]}{1 + k_{12}\tau[D] + k_{21}/k_{23}} , \qquad (52)$$

where $\alpha_{fi} = k_d/(k_d + k_1)$ is the probability of the formation of free ions from the radical-ion pair. Two extreme cases must be considered.

1. The electron transfer is slow, i.e. $k_{21}/k_{23} \gg 1$. We then obtain

$$L_0/L = 1 + k_{12}k_{23}\tau[D]/k_{21} , \qquad (53)$$

$$\gamma_{fi} = \alpha_{fi}k_{12}k_{23}\tau[D]/k_{21} . \qquad (54)$$

2. The electron transfer is rapid, i.e. $k_{21}/k_{23} \ll 1$. We then have

$$L_0/L = 1 + k_{12}\tau[D] , \qquad (55)$$

$$\gamma_{fi} = \frac{\alpha_{fi}k_{12}\tau[D]}{1 + k_{12}\tau[D]} . \qquad (56)$$

We may note that for long lifetimes of A* ($\tau > 10^{-7}$ s) and for high values of the product $k_{12}[D] \geq 10^8$ s^{-1}, we have $k_{12}\tau[D] \gg 1$ and $\gamma_{fi} = \alpha_{fi} = k_d/(k_d + k_1)$, i.e. the quantum yield in the formation of free ions is equal to the probability of the formation of such ions from the radical-ion pair. This is the highest possible value of γ_{fi}.

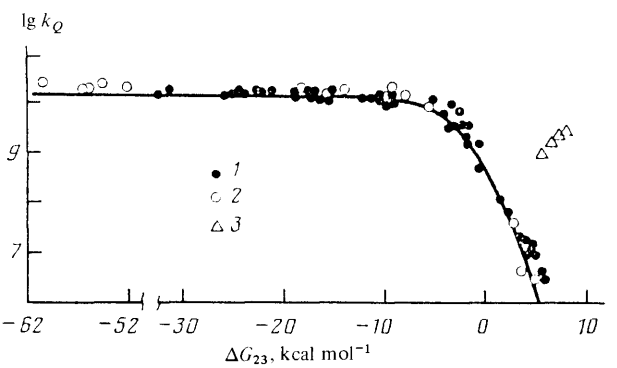


Figure 8. Dependence of the fluorescence quenching constant on ΔG_{23}: 1) electron acceptor in an excited state; 2) electron donor in an excited state; 3) transfer of a hydrogen atom.[48]

There is an interesting relation between the free energy of the electron transfer ΔG_{23} and the logarithm of the quenching constant $\lg k_Q$. The electron transfer rate constant k_{23} can be formulated in the usual form:

$$k_{23} = B_{23}\exp(-\Delta G_{23}^{\neq}/RT) , \qquad (57)$$

where B_{23} is a constant. According to Eqn.(44), $\Delta G_{23}^{\neq}$ is related to the free energy of electron transfer ΔG_{23}. The relation between these quantities can be most simply represented in the form of the linear Brønsted–Polanyi relation:

$$\Delta G_{23}^{\neq} = b + \beta\Delta G_{23} \qquad (58)$$

where b and β are constants for the given series of isotypical reactions. Thus Eqn.(57) can be written in the form

$$k_{23} = B\exp(-\beta\Delta G_{23}/RT) , \qquad (59)$$

where B is a new constant. Together with Eqn.(51), we obtain

$$k_Q = \frac{k_{12}B}{B + k_{21}\exp(\beta\Delta G_{23}/RT)} . \qquad (60)$$

For high negative values of ΔG_{23}, namely $\Delta G_{23} \leqslant -32$ kJ mol^{-1}, $k_Q = k_{12}$ follows from Eqn.(60). For positive values of ΔG_{23}, when the second term in the denominator is much greater than B, we obtain

$$\lg k_Q = \text{const} - 0.434\beta\Delta G_{23}/RT. \quad (61)$$

Fig.8 presents the dependence of $\lg k_Q$ on ΔG_{23},[48] where $\beta = 0.63$ (Bagdasar'yan[49]) and $k_{12} = 2 \times 10^{10}$ litre mol^{-1} s^{-1} (diffusion constant). The relation illustrated in Fig.8 is very general and has been established for many systems with electron transfer.[45]

2. The Absolute Rate Constants for the Formation and Dissociation of Radical-ion Pairs

In the previous Section we considered conditions determining the kinetics of the formation of geminate radical-ion pairs. The rate constant for the formation of radical-ion pairs in an encounter in space is defined by the Debye formula,[7] which is obtained from Eqn.(14) for the diffusion flux by adding to the right-hand side the term which defines the flux of point particles to a spherical surface $4\pi x^2$ under the influence of Coulombic attraction (or repulsion) to the central ion. For unlike charges e_1 and e_2 in a medium with a dielectric constant ε, this flux is

$$(De_1e_2/kT\varepsilon x^2) \cdot 4\pi x^2,$$

where $e_1e_2/\varepsilon x^2$ is the Coulombic interaction force and D/kT the mobility of the ions expressed in terms of the diffusion coefficient by the Einstein formula. Thus, instead of Eqn.(14), we obtain

$$\Phi = 4\pi x^2 D \frac{dc}{dx} - 4\pi Dqc \ , \quad (62)$$

where $q = e_1e_2/\varepsilon kT$ and Φ is independent of x. Integration of this equation subject to the boundary conditions $c = 0$ when $x = R$ and $c = c_\infty$ when $x \to \infty$ leads to the expression

$$\Phi = \frac{4\pi RDqc_\infty}{(e^{q/R} - 1)R} = 4\pi RDpc_\infty \ , \quad (63)$$

where

$$p = q[R(e^{q/R} - 1)]^{-1}$$

is the correction to Smoluchowski's formula for the number of encounters. The quantity q/R is the ratio of the Coulombic and thermal energies and Φ/c_∞ represents the rate constant for the encounters of radical-ions.

Eigen[50] obtained an expression for the rate of diffusional dissociation from the condition for the diffusional equilibrium of radical-ion pairs:

$$4\pi RDp[A][D] = k_d[A \cdot D]_{eq} \quad (64)$$

The equilibrium concentration of the pairs is obtained from Eqn.(8) by introducing the Boltzmann multiplier $e^{-q/R}$, which leads to the equation

$$k_d = \frac{D}{R^2}\left(\frac{q/R}{1 - e^{-q/R}}\right) \ , \quad (65)$$

where the multiplier in brackets represents the correction to the diffusion dissociation constant D/R^2 of uncharged species. It is noteworthy that Eqns.(63) and (65) presuppose that the ions are separated by at least one solvent molecule.

3. Geminate Radical-ion Pairs

The behaviour of the geminate radical-ion pairs arising as a result of electron phototransfer has recently attracted much attention. The influence of magnetic field on the yield of particular final recombination products has been studied in a number of investigations. However, the kinetic constants of the elementary processes determining the behaviour of the radical-ion pairs have been found in only a few studies. We shall consider in greater detail some of the systems investigated.

1. Pyrene–aromatic amines.[47,51–55] On excitation of pyrene (Py) with a laser pulse in the presence of a high concentration (0.1 M) of dimethylaniline (D) in a polar medium (CH_3OH or CH_3CN), an exciplex in a singlet state $^1(Py.D)^*$ is formed. The subsequent processes in this system are indicated schematically below:

$$\begin{array}{l} Py + D \rightarrow {}^1(Py \cdot D)^* \longrightarrow Py + D \\ \quad\quad\quad\

yield of the free ions on the viscosity of the medium was established:[55] with increase of the viscosity by a factor of 25 (from 5.8 to 142 cP), the constant k_d decreased only by a factor of 4 (from 2.6×10^7 to 0.6×10^7 s^{-1}). Experimental data were anlaysed in the above study without taking into account the spin transitions.

2. Anthracene–dimethylaniline (D).[56] The anthracene in solution in acetonitrile was excited with light at $\lambda = 337$ nm (N_2 laser, duration of pulse 2.5 ns). At a dimethylaniline concentration of 0.1 M, the fluorescence of anthracene is fully quenched after only 1 ns, which leads to the formation of a radical-ion pair in the singlet state. The kinetics of formation of the triplet anthracene molecule ^3A were determined by probing the solution at $\lambda = 425$ nm (the absorption maximum of ^3A). The probing beam from a dye-based laser followed the exciting beam at different time intervals. In the absence of a magnetic field, the yields of the anthracene triplets were 4.8, 8.2, and 10.5% after 5, 7, and 15 ns respectively. After the application of a magnetic field, the yield of the triplets diminished and reached a limiting value in fields stronger than 150 G. Subject to certain assumptions, agreement was achieved between the experimental data and the theory of spin evolution induced by hyperfine interaction.[53]

3. Fluorenone–diazabicyclo-octane in propylene carbonate.[57] Under the influence of light at $\lambda = 347$ nm (ruby laser), a triplet fluorenone molecule and then a radical-ion pair in the triplet state are formed. Optical absorption by the fluorenone triplets at 425 nm was measured immediately after the laser pulse and when 2 μs had elapsed, measurements were also made of the absorption by the fluorenone radical-anions at 540 nm. The fraction of the triplet radical-ion pairs which have dissociated into ions was determined from these data. The viscosity of propylene carbonate was varied from 1 to 100 cP by varying the temperature from 213 to 343 K. In this range of viscosities the yield of free ions α_{fi} changed from 0.13 to 0.89. It was assumed that the free ions are formed on dissociation of the triplet pair and that the recombination (reverse electron transfer) takes place in the singlet pair after the change in the spin state of the pair. Thus $\alpha_{fi} = k_d/(k_d + k_S)$ and, after the application of a magnetic field, $\alpha^H_{fi} = k_d/(k_d + k^H_S)$. The influence of the magnetic field can be represented in the form $(\alpha^H_{fi} - \alpha_{fi})/\alpha_{fi}$. This ratio increases from 1.5% to 23% with increase of the viscosity of the medium from 1 to 45 cP ($H = 270$ G). After the application of the magnetic field, the T_+ and T_- sublevels are disconnected, which decreases the probability of the transition from the triplet to the singlet pair and increases the probability of the competing process—the dissociation of the triplet pair into free ions.

The dependence of the probability of recombination $\phi = 1 - \alpha_{fi}$ on the viscosity of the medium has also been examined by the Noyes method.[57] The application of the diffusion gradient method makes it possible to estimate the constant k_S. Fig.9 illustrates the dependence of $1/\alpha_{fi}$ on η/T according to the data of Periasamy and Linschitz:[57] $k_S = 3 \times 10^8$ s^{-1} follows from the slope.

4. Pyrene–dicyanobenzene (A) in various solvents.[58] Excitation with a laser pulse at $\lambda = 347$ nm results in the formation of the radical-ion pairs ($Py^+.A^-$). The kinetics of the formation and destruction of the radical-ion pairs and the free Py^+ ions were followed spectrophotometrically at 445 nm (the absorption maximum of Py^+), while the kinetics of the formation and destruction of the free ions alone were followed conductimetrically (for several hundreds of nanoseconds). In solutions in acetonitrile ($\varepsilon = 38$) the maximum photocurrent is obtained immediately after the termination of the pulse and then diminishes slowly as a consequence of volume recombination. With decrease of ε of the solvent, the maximum photocurrent is attained after a longer time as a consequence of the decreased rate of dissociation of the radical-ion pairs. For liquids of average polarity ($\varepsilon = 9$–12), the experimental rate of formation of free ions approximately agrees with the rate of dissociation of the radical-ion pairs calculated by Eqn.(65).

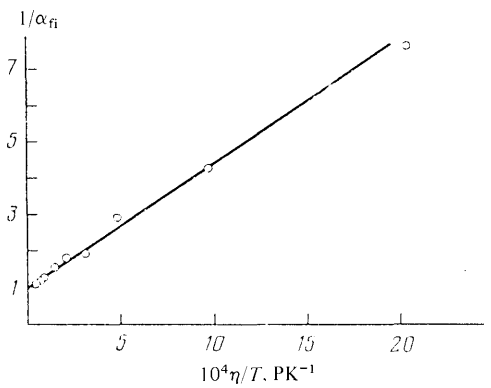


Figure 9. Dependence of $1/\alpha_{fi}$ on η/T according to the data of Periasamy and Linschitz.[57]

5. The

$Ru^{2+}(bpy)_3$ – methylviologen $\left(CH_3-\overset{+}{N}\!\!\bigcirc\!\!-\!\!\bigcirc\!\!\overset{+}{N}-CH_3\right)$.

system. This system has been the subject of numerous investigations in connection with the problem of the photochemical utilisation of solar energy, since, on illumination with visible light, it is thermodynamically feasible for the system to allow the decomposition of water into hydrogen and oxygen.[49] The primary reaction leads to the formation of a radical-ion pair (MV^{2+} = methylviologen):

$$Ru^{2+}(bpy)_3^* + MV^{2+} \rightarrow [Ru^{3+}(bpy)_3 \cdot MV^+] \begin{cases} \xrightarrow{k_1} Ru^{2+}(bpy)_3 + MV^{2+} \\ \xrightarrow{k_d} Ru^{3+}(bpy)_3 + MV^+ \end{cases}.$$

The radical-ion pair either recombines or dissociates with formation of the free ions MV^+ and $Ru^{3+}(bpy)_3$, which, in the presence of catalysts, are capable of inducing the evolution of hydrogen and oxygen respectively from water.

The yield of free ions from the radical-ion pairs, i.e. the quantity $k_d/(k_d + k_1)$, has been determined[59] by the method of nanosecond photolysis ($\lambda = 530$ nm). A characteristic feature of this system is the long lifetime of the excited $Ru^{2+}(bpy)_3^*$ molecules (several hundreds of nanoseconds), during which pairs are continuously generated and destroyed. The concentration of the radical-ions MV^+ released into space is related to the concentration of $Ru^{2+}(bpy)_3^*$ formed during the pulse in the following manner:

$$[MV^+]_\infty = [Ru^{2+}(bpy)_3^*] \frac{k_2[MV^{2+}]}{k_0 + k_2[MV^{2+}]} \frac{k_d}{k_d + k_1}, \qquad (66)$$

where the first fraction represents the probability of the reaction of $Ru^{2+}(bpy)_3^*$ with MV^{2+} [k_0 is the rate constant for the spontaneous deactivation of $Ru^{2+}(bpy)_3^*$]. All the necessary quantities were determined experimentally. Thus the

probability of the relase of the radical-ions into space from the radical-ion pairs was determined from Eqn.(66); it amounts to 0.22 for an aqueous solution and to 0.17 for an aqueous glycerol solution (η = 3.3 cP).

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The application of diffusion kinetics to the description of homogeneous molecular processes began with the studies of Vavilov and co-workers (1928–1929), who based their treatment on the diffusion theory of the rapid coagulation of colloids proposed by Smoluchowski (1918). These studies led to the development of the diffusion gradient method for the description of the recombination of radicals and other barrier-free processes. Franck and Ravinowitch (1934) put forward the concept of the "cage" in which a "pair" of radicals arising in the photochemical or thermal dissociation of the molecules is enclosed. In Noyes' studies (1955–1961) the pair was regarded as a dynamic system whose behaviour is described by the microscopic parameters of molecular movement. Subsequently a quantitative description of the cage effect based on phenomenological kinetic parameters was achieved using the gradient diffusion method. This led subsequently to the concept of contact or "almost" contact pairs as intermediate species in radical-barrier free reactions.

The discovery of the spin and magnetic effects in radical pairs is a new important stage in a development of our ideas about the recombination of radicals. Soviet scientists have made a considerable contribution to the development of these ideas. The creation of a rigorous quantitative theory of the recombination of radicals taking into account the spin and magnetic effects and the molecular movements of radicals constitutes a very complex problem. An important step in this direction was made as a result of studies published recently.[60,61]

An approximate method, which the author of the present review called the approximation of chemical kinetics, has been widely used in experimental studies on the recombination of radicals. The phenomenological rate constants for various elementary processes, including diffusion and spin processes, which together determine the behaviour of the radical pairs, are used in this method. These constants can be found from experimental data.

The theory of radical recombination is still far from being complete. The experimental data considered in this review indicate an appreciable difference between the kinetic constants for geminate pairs and the pairs formed in the enounters of the same radicals in space. The discrepancy is apparently associated with the characteristic features of the formation and behaviour of the geminate pairs. It is undoubtedly essential to take into account the rotational diffusion of the radicals forming the contact or "almost" contact pairs, to which attention has been drawn in the present review. The recombination and dissociation of the radical-ion pairs and their dependence on the viscosity of the medium have been inadequately studied. The Debye–Smoluchowski [Eqn.(63)] and Eigen [Eqn.(65)] equations have received little experimental confirmation for organic radical-ions. Thus this field of chemical kinetics requires further studies—both experimental and theoretical.

The behaviour of geminate electron–radical-cation pairs, which were mentioned in the Introduction, is of considerable interest. The properties of these pairs to a large extent determine the chemical reactions occurring under the influence of ionising radiation on liquid media. A convenient method for the study of these pairs is two-quantum photoionisation (see the present author's earlier review[62]). The high mobility of electrons in the liquid medium results in a significant difference between an electron–radical-cation pair and a radical ion pair. The properties of geminate electron–radical-cation pairs therefore require separate consideration.

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Karpov Physicochemical Institute,
Moscow

Translated from *Uspekhi Khimii*, 53, 1101-1124 (1984) U.D.C. 541.67:541.142

The Structural Chemistry of Crystalline Carbon: Geometry, Stability, and Electronic Spectrum

I.V.Stankevich, M.V.Nikerov, and D.A.Bochvar

The crystalline modifications of carbon described in the literature are briefly reviewed. The publications in which new types of structures, differing from the diamond and graphite lattices, are proposed and discussed are analysed in detail. The geometrical-topological characteristics of the hypothetical modifications of carbon, their relative stabilities, the nature of the chemical bonds, and the structure of the electronic spectra are discussed.
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I. INTRODUCTION

The carbon atoms forming part of the composition of hydrocarbon molecules stable under normal conditions can form chemical bonds with two, three, or four neighbours. As a rule in the first case the carbon atom and two of its partners are located on a single straight line, in the second case they form a planar molecular fragment with valence angles close to 120°, and in the third case a nearly tetrahedral disposition of the bonds is achieved. These features can be described in terms of the hybridisation theory, according to which carbon atoms tend to form directed two-centre σ-bonds with participation of sp-, sp^2-, and sp^3-hybrid orbitals; in the first two cases there is a possibility that additional bonds of the π-type may arise.

The numerous structural data for saturated and unsaturated hydrocarbons can be interpreted fairly reliably within the framework of the terms described above. Extended molecular systems in which carbon–carbon bonds are formed preferentially are of special interest. In the limit such systems can be regarded as infinite and consisting of carbon atoms only and can be divided into two groups: (1) systems made up of carbon atoms or small clusters of the latter having a regular structure in which the positions of the atoms or the clusters can be random; (2) systems in which the atoms are distributed regularly in three dimensions and form a complex bonded system with translational invariance. For example, carbon black, vitreous carbon, and various amorphous carbon films belong to the first, non-crystalline type, while crystals such as those of diamonds (cubic and hexagonal) and graphite (hexagonal and rhombohedral) belong to the second type.

Diamond and graphite are examples of extended systems in each of which sp^3 and sp^2 hybridisation obtains respectively; sp hybridisation arises in carbyne, which consists of linear macromolecules according to the investigators[1,2] who discovered this new allotropic form of carbon.

Together with diamond and graphite, whose structures have been thoroughly investigated, several other crystalline modifications of carbon have been described in the literature: up to eight carbyne forms, metallic carbon, C_8 carbon, etc., whose structures have not so far been established or have not been demonstrated sufficiently reliably.[3–6] The hypothesis has been put forward[7] that certain metastable carbon phases of unknown structure can arise in the growth of carbon layers on various crystalline modifications of boron nitride.

The modelling of the structure of amorphous carbon is an extremely complex problem and is extremely important for the interpretation of the physicochemical properties of the substance and for the creation of carbon materials with specified properties. In setting up a model of amorphous carbon, one usually employs the structural fragments of known crystalline modifications of carbon. For example, a model has been proposed[8] for the interpretation of the structure of sputtered amorphous carbon films according to which the structure of such a film can be represented as a bonded formation consisting of fragments of diamond-like and graphite-like types. The deficiencies of this model have been noted[9] and it has been emphasised that the earlier investigation[8] did not take into account the possibility of the formation of non-diamond-like and non-graphite-like fragments. Apparently the unsuitability of this model for the description of the structure of low-density carbon films is associated with this factor. The data quoted[9] also show that the most probable interatomic distance in the specimens obtained is intermediate between the lengths of single and double bonds; furthermore, the presence of multiple bonds is emphasised. A detailed analysis of experimental studies and model ideas used at the present time for the description of the structure of polymeric carbon has been carried out in a review.[10]

The existence of crystalline modifications of carbon of unknown structure, the difficulties arising in the modelling of the structure of amorphous carbon, and also the search for new carbon materials with a specified set of properties have led to the formulation of several theoretical problems which we believe to be extremely acute for the physical chemistry of carbon. It is necessary to discover whether the entire family of crystalline modifications of carbon is exhausted by the three forms described above—diamond, graphite, and carbyne, and, if not, what are the possible structures of these other hypothetical forms of carbon. It is also necessary to consider what evidence can be adduced in support of the possibility of the existence of such forms and what could be the physicochemical properties of these systems. This paper has been devoted to the analysis of the present state of these problems, which have been hardly discussed in the review mentioned above.[10]

II. CRYSTALLINE MODIFICATIONS OF CARBON DESCRIBED IN THE LITERATURE

There are two polytypical modifications of diamond: cubic diamond (D_c), which belongs to the $Fd3m$ symmetry space group and whose unit cell contains eight carbon atoms, and hexagonal diamond (D_h)—lonsdaleite, which belongs to the $P6_3/mmc$ symmetry space group and whose unit cell contains four carbon atoms.[11,12] The physical properties (density, hardness, electrical resistivity, and optical properties) of D_c and D_h are very similar, which is due to the identity of the first layer around each carbon atom in these diamond modifications; the valence angles are 109°28′16″ in both, the bond lengths are close to 1.545 Å, and the coordination number of each carbon atom is four. The difference between the second layers surrounding the carbon atoms in cubic diamond and in lonsdaleite is due to the fact that in cubic diamond all the layers made up of coordination tetrahedra are oriented in the same manner, while in lonsdaleite each succeeding tetrahedral layer is rotated by 60° relative to the previous layer.[13] Fragments of the crystal structures of D_c and D_h are presented, for example, in a monograph.[12]

The cubic modification of diamond is thermodynamically stable, being more stable than graphite at sufficiently high pressures, but it also exists at low pressures in a metastable state. The transformation of diamond into graphite takes place with a change in the first coordination sphere and in the type of chemical bond, which is the reason for the high energy barrier to the transformation and the low rate of the process. Lonsdaleite is a metastable modification of carbon; at high pressures it is transformed into cubic diamond and at low pressures into graphite. The phase transformations in carbon have been described in detail.[11,14]

Each carbon atom in diamond forms four stable covalent bonds with neighbouring carbon atoms and all the bonds are equivalent. The equivalence of the bonds in diamond makes it possible to employ the approximation of equivalent orbitals in the calculation of its band structure. The equivalent orbitals are linear combinations of atomic wave functions which are interconverted under the influence of the operations of the symmetry group of the crystal; this reduces the number of independent matrix elements and makes it possible to obtain the dependence of the energy of the molecular orbitals on the wave vector along symmetrical directions in the inverse space in an analytical form. The methods for the calculation of the electronic structure of crystals with the diamond structure have been considered in detail in a monograph.[15] The applicability of the method of equivalent orbitals to the description of the band structure of diamond indicates the localised character of the bonds in diamond, since the method of equivalent orbitals is particularly successful in a description of structures with localised bonds.

The second allotropic modification of carbon is graphite, which also exists in the form of two polytypic forms: hexagonal graphite (G_h) with a $P6_3/mmc$ symmetry group and four carbon atoms in the unit cell and rhombohedral graphite (G_r) which has a $R\bar{3}m$ symmetry space group and six carbon atoms in the unit cell.[11,12] Graphite has a layer structure and consists of hexagonal carbon layers linked by van der Waals forces. The structures of the layers in G_h and G_r are almost identical (the coordination number of carbon is three, the bond lengths are close to 1.42 Å, and the valence angles are 120°). However, the arrangements of the layers in these two modifications are different, which also leads to a difference between their crystal structures.[11,16] In hexagonal graphite each third layer repeats the first and each second layer is displaced relative to the first in such a way that half the atoms of each layer are located respectively above and below the centres of the hexagons of the neighbouring layers. The sequence of identical layers in G_h can be represented conventionally by the symbol ...ABABAB.... In rhombohedral graphite each fourth layer repeats the first. The sequence of the layers in G_r can be represented by the symbol ...ABCABC.... In several processes rhombohedral graphite always occurs in specimens of natural origin and in the products of the mechanical treatment of graphite.[16] The high degree of anisotropy of the physical properties of graphite (electrical conductivity and optical and thermal properties) is associated with the fact that the interaction between the hexagonal layers in graphite is much weaker than the interaction within each layer (the distance between the graphite layer is 3.35 Å); the physical properties of G_h and G_r are similar.

Of the four valence electrons of each carbon atom in graphite, three are involved in the formation of localised σ-bonds with neighbouring atoms. The fourth valence electron is located in the $2p$ orbital whose symmetry axis is at right angles to the plane of the hexagonal layer and participates in the formation of bonds of the π-type, which make up an extended delocalised π-electron system. The orthogonality of the orbitals of the electrons in the σ- and π-systems makes it possible to obtain the principal qualitative characteristics of the bands in the spectra of graphite in terms of the π-electron approximation, where only one $2p$ electron of each atom is taken into account and it is assumed that these mobile π-electrons migrate in the field of a rigid σ-skeleton.

Since the interaction between the layers of graphite, which is of the van der Waals type, is fairly weak, a two-dimensional model is frequently employed in the calculation of the band structure of graphite. The two-dimensional model leads to a zero width of the energy gap between the valence and conductivity bands and to a marked anisotropy of the properties of graphite, which agrees with experiment and the results obtained for the three-dimensional model. In order to achieve a quantitative agreement between theory and experiment, it is necessary to take into account also the interlayer interaction. The properties of graphite have been described by Ubbelohde and Lewis[16] and the methods for the calculation of its band structure have been described, for example, by Slonczewski and Weiss[17] and Ovchinnikov and Belyi.[18]

The principal properties of graphite and diamond have so far been adequately described in theoretical terms and the main efforts in this field are therefore nowadays directed to the study of diamond-like and graphite-like systems with less perfect and more indefinite structures (the influence of defects, the formation of layer compounds of graphite with various metals, the description of the band structure and properties of non-graphitised carbon, etc.), as well as the interconversions of the modifications of carbon and the conditions governing their formation.[11,16,19,20] Furthermore, diamond and graphite can be regarded as model systems on which it is possible to test various new methods and approximations of solid state physics and quantum chemistry.

As mentioned above, apart from diamond and graphite, there exist also other crystalline modifications of carbon whose structure is so far unknown or has been studied with inadequate reliability. In 1979 the synthesis of new cubic modifications of carbon with the $Im3$ symmetry space group and containing sixteen carbon atoms in the unit cell was reported.[5] The new crystalline modification of carbon, called by the authors C_8, was obtained by condensing fluxes of carbon plasma on cooled supports; C_8 is formed in the form of single crystal inclusions, whose size is up

to 3000 Å, in a carbon film. The theoretical density of the new modification $\rho = 4.1$ g cm^{-3}, i.e. is greater than the density of diamond (3.51 g cm^{-3}); the microhardness of C_8 exceeds that of diamond, the coordination number is 4, and the period of the body-centred lattice is 4.28 Å. This modification of carbon consists of coordination tetrahedra[21] of the same kind as in D_c and D_h but somewhat deformed and more closely packed. The valence angles in the C_8 modification differ from the tetrahedral values (90° and 125°16′), while the bond lengths are also different and greatly reduced (1.42 and 1.23 Å).

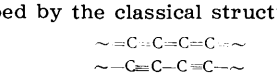
The structure of C_8 can be represented as a result of the polycondensation of cubane C_8H_8,[22] in which hydrogen is competely removed and the vertices of the carbon cubes are linked by chemical bonds. The bond lengths between the vertices of individual cubes are 1.23 Å, which is close to the lengths of the triple bond in acetylene; however, the C–C bond length in cubane is 1.55 Å.[23] The combination of a coordination number of 4 and bond lengths of 1.42 and 1.23 Å in C_8 is not altogether usual and conflicts with the empirical rules established for bond lengths in molecules,[24] according to which bond lengths of approximately 1.54 Å are characteristic of a carbon atom forming four bonds. Certain diffraction lines in the X-ray diffraction patterns, close to those found[5] for C_8, have been observed for the carbon particles obtained as a result of the exposure of octane, decane, and iso-octane drops to a laser beam.[25] Nevertheless the deviation of the bond length in C_8 from the classical values shows that the crystal structure of C_8 requires additional experimental confirmation.

The report[6] of the preparation (as a result of the impact compression of a graphite single crystal up to pressures in excess of 150 kbar) of a modification of carbon, which is metastable at atmospheric pressure and which has a cubic lattice with a period of 5.545 Å and 24 atoms in the unit cell, has also not been finally confirmed. The individual interplanar spacings, determined in the above study,[6] are encountered in carbon powders obtained on crystallisation of carbon from the gas phase and also in the same powders subjected to high pressures and temperatures corresponding to the region of stability of diamond.[26] The symmetry space group of this modification has not been established. The authors[6] merely quote a set of space groups compatible with the observed diffraction lines. The density of the modification is 2.8 g cm^{-3}, i.e. is intermediate between the densities of diamond and graphite (2.265 g cm^{-3}).[16]

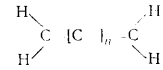
The phase diagram of carbon, in which a region of the thermodynamic stability of solid metallic carbon (carbon III) had been noted at high pressures ($p > 600$ kbar), was published in 1963.[27] The preparation of metallic carbon has been reported in another study,[4] but its structure had not been determined. The present ideas concerning the phase diagram of carbon have been described in detail by Bundy.[28]

Apart from the communications enumerated above concerning new crystalline modifications of carbon, there have been numerous studies devoted to crystalline modifications of carbon of the carbyne type. Up to eight modifications of carbyne are now known[3] (α-carbyne, β-carbyne, etc.), but the crystal structures of none of them have so far been established.

According to some investigations,[1–3,29,30] carbyne is a crystalline modification of carbon consisting of fairly long (number of carbon atoms approximately 10^3) linear carbon chains weakly interacting with one another. In the ideal case, there is a possibility of two carbyne forms, which can be described by the classical structural formulae



The end groups are not represented in these systems, although in fact such groups are extremely important for the understanding of the structural differences between these compounds. In the first case the macromolecule has the form



(I)

and is of the cumulene type. In the second case the macromolecule is of the poly-yne type:



(II)

In the case of purely carbon macromolecules, a structure of an intermediate type should obtain.

Raman spectroscopic data[31] indicate the presence in the spectrum of the mineral chaoite[32] of a band at 2140 cm^{-1} corresponding to the stretching vibrations of the triple bond $-C\equiv C-$; however, this fact alone is insufficient to conclude that the molecules of chaoite let alone those of all the carbyne modifications of carbon are linear. Henceforth carbyne will be understood as a modification of carbon with a linear structure of its constituent macromolecules and as crystalline modifications of carbon whose structure has not been established and which have been classified as carbyne forms of carbon; however, in the future it may turn out that certain carbyne modifications of carbon known at present do not consist of linear molecules. The proposed agreement concerning terminology is justified by the fact that the term "carbyne" has penetrated the literature extensively and is used both in relation to model systems consisting of linear carbon macromolecules[33–36] and in relation to crystalline modifications of carbon whose structure has not been established with adequate reliability or is unknown.[1–3,25,26,29,37,38]

The methods used to prepare carbyne are extremely varied: synthesis from acetylene;[30,39] deposition of carbon vapour, obtained on sublimation of graphite by a laser beam, onto a glass or other support;[40] the formation of a white film of carbyne when an electric current is passed through a graphite rod;[41] plasma-chemical methods;[42,43] etc.[44,45] Unfortunately a single crystal of carbyne sufficiently large for the elucidation of its crystal structure cannot be obtained by any of these methods. Single crystals of carbyne (chaoite), discovered in a meteorite crater,[32] in natural graphite deposits,[37] and in a meteorite[46] are also too small to determine their crystal structure.

The data obtained in the study of carbyne modifications of carbon lead to the following ideas about its structure and properties. Carbyne is a white substance[32,37,41,47] with an almost 100% content of carbon, whose density is intermediate between those of diamond and graphite, and which is chemically resistant to oxidants and other reagents.[48] Carbyne single crystals with dimensions up to 10^4 Å have hexagonal symmetry[1,2,32,38] and the unit cell contains a large number of carbon atoms (for example 144 for α-carbyne and 72 for β-carbyne[1,29]), which hinders the determination of its crystal structure from diffraction data. According to Whittaker,[3] the region of thermodynamic stability of carbynes is at temperatures from 2600 to 3800 K. On heating (by an electric current in an atmosphere of argon), graphite is slowly converted into linear forms of carbon, the reverse process occurring rapidly on cooling.[49] At pressures greater than 60 kbar, the carbyne forms of carbon are converted into diamond-like structures and, on reducing the pressure to 0 2 atm and less, carbyne sublimes.

According to some data,[26,50,51] the β-modification of carbyne is more stable at high pressures, while the α-modification is more stable at lower pressures. Some

data on the heat capacity of carbyne[52] indicate the quasi-one-dimensionality of its molecules but at the same time there have been reports[1,54] that, as a consequence of the high reactivity of the carbon chains, it is very difficult to avoid the formation of chemical bonds between them (with increase of their length) during the preparation of carbyne chemically. It may be that, as a consequence of this, in the synthesis of carbyne the final product always contains a definite number of bonds between the chains whose positions cannot be determined by X-ray and electron diffraction.

Overall, the available information about the physical properties of carbyne is fairly scanty, which leads to arbitrary theoretical constructions and estimates concerning carbyne, since the present state of the methods for the calculation of the electronic and crystal structures of solids precludes a reliable prediction of any one property of the solid without resorting to experimental data. At the same time, it is essential to note that most investigators have no doubt about the existence of crystalline modifications of carbon of the carbyne type because X-ray and electron diffraction methods lead to structural parameters of carbyne which are definitely different from those of diamond and graphite.[1,29,47,54,56] Furthermore, photoelectron spectroscopic data[55] also indicate significant differences between the spectra of diamond, graphite, and carbyne. Apparently carbyne has a characteristic ionic spectrum (the ratio of the concentrations of the C_2^- and C_6^- ions),[49,57] which makes it possible to employ ionic spectrometry for the detection of microinclusions of carbyne in carbon specimens of natural and artificial origins.

We may note that, in the literature devoted to theoretical studies of the electronic structure of carbyne, for example, in the communication of Misurkin and Ovchinnikov,[58] the activation energy for electrical conduction in carbyne, obtained from the measurement of the temperature variation of the electrical conductivity, is quoted as $\Delta E = 1-2$ eV and this value is identified with the width of the forbidden gap in carbyne $\Delta\varepsilon$. However, in another investigation[59] the conductimetric measurements were performed on a specimen consisting of a black insoluble powder containing 98% of carbon and obtained by the polycondensation of acetylene. At the same time it is known that in other methods of synthesis the carbyne forms of carbon are white and contain almost 100% of carbon. The activation energy for electrical conduction in the black specimen must have been influenced by admixtures and the boundaries between the grains, so that these data[59] concerning ΔE can hardly be correctly attributed to carbyne forms of carbon. The white colour of the carbon films is more probably an indication that the width of the forbidden gap in the electronic spectrum of carbyne is greater than the maximum energy of the photon in the optical range, which is 3.3 eV.

The carbyne macromolecules have been investigated by various quantum-chemical methods: in the π-electron approximation, in the valence approximation, and taking into account all the electrons. Special interest in this branch of the quantum chemistry of polymers arose in the second half of the 1960's [30] when it was suggested that carbyne consists of linear carbon chains or of fairly long hydrocarbon molecules of types I and II. The real differences between systems I and II are manifested primarily in the geometry, which in the case of system (I) depends on the parity of the number n. The carbon skeletons of the molecules of (I) and (II) are linear. In the former case the C–C bond lengths are identical and close to 1.3 Å, while in the latter case they alternate and the extent of this alternation apparently depends little on n.

The electronic spectra of systems (I) and (II) are also different. The energy of the first transition for the molecule of the cumulene type tends to zero, while in the case of the poly-yne system there is a forbidden gap whose width is non-zero.[60–63] For small values of n, the influence of the end groups on the C–C bond length is extremely significant. Calculations for a series of compounds C_4, C_4H_2, C_4H_4 and C_6, C_6H_2, C_6H_4 have been carried out[64] in terms of the valence approximation by the extended Hückel method (EHM) using Cusachs' parametrisation[65] with partial optimisation of the geometry; in the case of the C_4H_2, C_4H_4, and C_6H_2 molecules the calculations led to results close to the experimental data. Qualitative estimates of the C–C bond length in the linear C_4 and C_6 molecules have been made on the basis of these calculations.

Results indicating an appreciable influence of the end effects on the geometrical characteristics of the inner parts of the molecules of the given type, containing a fairly large number of carbon atoms, have been obtained.[66] The same communication[66] presents results of quantum-chemical calculations for molecules of the types C_nH_2, C_nH_4, and C_n (linear configuration) with $n \leq 18$ in the valence approximation of the EHM. A model was used in which it was assumed that the distance r between the carbon atoms is related to the corresponding bond population (Mulliken population) p by the expression

$$r = 1.860297 - 0.54869p + 0.109747p^2$$

found on the basis of calculated data for acetylene, benzene, ethylene, and ethane.

The calculation in the above study[66] was iterative. Hoffmann[66] analysed in detail the disadvantages of this model and noted in particular that the agreement in terms of the bond orders may not correspond to the total energy minimum. However, the bond lengths found for a small value of n proved to be close to the experimental lengths (allene, butatriene, diacetylene, triacetylene) and this factor served to some extent as justification of the possibility of employing this approach for high values of n. The results of Hoffmann's calculations[66] led to the conclusion that the influence of the end groups on the bond lengths in the C_n, C_nH_2, and C_nH_4 molecules is extremely significant, at any rate for $n < 20$.

In order to solve the question of the possible existence of fairly long molecules of the type C_nH_2, C_nH_4, and C_n, a whole series of quantum-chemical calculations were performed for model linear systems of the C_n type consisting of a large number of carbon atoms. These calculations were performed in terms of different approximations: at the π-electron level taking into account the influence of the σ-skeleton by an additive scheme, taking into account all the valence electrons (EHM, CNDO/2, and the method of a three-dimensional electron gas), and by non-empirical methods.[34–36,67–73] In some of these studies[67–72] Bloch's cyclic model was used. The possibility of the alternation of the lengths of neighbouring C–C bonds (r_1 and r_2) was assumed. The average total energy per elementary fragment (in the given case the elementary fragment consists of two carbon atoms) was regarded as a function of two independent parameters and was optimised. All these calculations led to the same qualitative conclusions regardless of the approximation employed: the minimum average potential energy of the $^\sim C_n$ system in the limit at $n \to \infty$ is reached when $r_1 \neq r_2$ and the C_∞ system is stable in relation to dissociation into diatomic fragments.

On the one hand, the conclusion of the alternation of the bond lengths is satisfactorily consistent with the Peierls theorem, which states that one-dimensional systems with

an energy spectrum of the metallic type are unstable, since the alternation of the bond lengths automatically leads to the appearance of a gap in the spectrum, which is manifested even in the Hückel π-electron approximation. On the other hand, it has been shown in a number of studies that, in terms of the π-electron approximation, when account is taken of the correlation effects, the width of the gap is not zero also when the bond lengths are equal ($r_1 = r_2$, see, for example, the relevant reviews[58,74]). It has been concluded[58] that in cumulene chains with a sufficiently large number of carbon atoms an antiferromagnetic state obtains and for this reason the bond lengths may be identical in long cumulene molecules far from the ends. However, we may note that this conclusion has been reached in terms of the π-electron approximation.

In conclusion one should note that, from our point of view, the use of the average value of the total energy for the estimation of the local geometrical properties of the molecule is an unduly rough approximation: the model leads *a priori* to an average bond length and for this reason the average total energies of the C_n, C_nH_2, and C_nH_4 systems with the same geometry of the carbon skeleton tend to the same limit and caution must be exercised in interpreting the results obtained within the framework of this model However, the conclusions reached in a number of studies[67-72] do not conflict with the possibility of the existence of fairly long molecules of the type C_n, C_nH_2, and C_nH_4. At the same time, the high reactivity of such systems can lead to the presence of intermolecular cross-links and, in order to avoid them, it is necessary to isolate the molecules from one another in some way. One of such procedures, associated with the synthesis of carbyne forms of carbon from tetrafluoroethylene, has been discussed.[75]

III. HYPOTHETICAL CRYSTALLINE MODIFICATIONS OF CARBON

1. The Geometrical-Topological Properties of Crystalline Carbon and Certain Energy Estimates

Diamond and graphite are two allotropic crystalline modifications of carbon which differ from one another both in the type of structure and in the coordination numbers of the atoms.[12] The structures of diamond and graphite are free from strain, since their valence angles agree with the classical angles for tetracoordinate and tricoordinate carbon atoms respectively. All the bonds in diamond are equivalent and the carbon atoms are located in structurally equivalent positions. To within fairly weak interlayer interactions, the positions of the atoms in graphite are also equivalent; the bonds in the graphite layer are equivalent to one another also when account is taken of the interlayer interactions. The characteristic features of the diamond and graphite structures enumerated above (the equivalence of the bonds and of the positions of the atoms, the absence of strain) distinguish them from the multiplicity of the remaining modifications of carbon listed above; apparently these features are responsible for the stability of diamond and graphite and their wide occurrence in nature.

If the macromolecules of carbyne have a linear structure, then its valence angles should be 180°, which also leads to the absence of strain, because an angle of 180° is characteristic of the dicoordinate carbon atom. In a structure of the cumulene type, the C–C bonds are equivalent and all the atoms occupy equivalent positions, provided that, as in graphite, one neglects their intermolecular interaction. In a structure of the poly-yne type, the equivalence of the bonds breaks down, but a linear chain of the poly-yne type is also free of strain. The deviations of the structural type of carbyne and of the coordination number of atoms in it from the corresponding characteristics of diamond and graphite make it possible to regard carbyne as the third allotropic crystalline modification of carbon.

We shall now consider the question whether there is a possibility of further crystalline modifications of carbons free from strain. Such a possibility will be considered in a purely geometrical sense and the identity of the valence angles with the classical values (109°28′16″, 120°, and 180° for tetracoordinate, tricoordinate, and dicoordinate carbon atoms respectively) will be regarded by convention as the criterion of the absence of strain.

The presence of chemical bonds between the carbon atoms in diamond and graphite makes it possible to describe naturally the structures of these compounds in terms of regular networks. The term "net" is used in this review as a non-oriented graph with an infinite number of vertices located in a three-dimensional space at the points corresponding to the positions of the lattice atoms. The vertices are assumed to be adjacent when the interatomic distances do not exceed 1.6 Å. In diamond the corresponding graph is connected and homogeneous and the degree of each of its vertices is 4. In graphite the graph is subdivided into an infinite number of subgraphs corresponding to individual layers. Carbyne can also be described in terms of an infinite number of subgraphs, each subgraph being linear. From the standpoint of the graph theory, the positions of the vertices and the lengths of the edges as well as their form are not significant. The problem of describing the possible crystalline modifications of carbon (CMC) is therefore a special case of the problem of describing infinite graphs satisfying the following properties: a graph must permit a geometrical construction in which the angles between the edges (in the given instance we consider the sections connecting the vertices) are identical with or close to the classical valence angles in the C–C bonds. Furthermore, the geometrical graph must have the property of periodicity and the number of atoms in the elementary fragment should not be very large.

Thus graph theory may be used for the description of structures which satisfy the essential requirements of valence theory for the carbon atom. We shall discuss initially the structures of the graphite-like type described by a system of unconnected graphs with a degree of 3, each of which can be represented in the plane as a periodic structure.

In connection with the problem of the existence of new crystalline modifications of carbon, this approach has already been used.[76] The authors of that investigation discussed mainly geometrical graphs with a mosaic structure made up of a combination of different carbon rings: four-membered and eight-membered, three-membered and twelve-membered, and also five-membered and seven-membered. Some of these planar systems are illustrated in Fig. 1. In all the structures there are extended π-electron systems. The valence angles deviate from 120°; the degree of each vertex of the graph is 3. For example, in the graph $(3:4,8^2)$ (Fig. 1*b*) two valence angles are 135° and the third is 90°. Here we have made use of a notation which is convenient for certain homogeneous graphs; the number 3 denotes the degree of the vertex and the numerals 4 and 8 represent the size of the rings to which each vertex belongs. In the graph $(3:4,8^2)$ each vertex belongs to one four-membered and two eight-membered rings, which is denoted

by the superscript 2 to the numeral 8. $(3:6^3)$ corresponds to a graphite layer (Fig. 1*a*) in terms of the same notation. Fig. 1*c* represents also a (3:5,7) net made up of five- and seven-membered rings. The deviation of the valence angles in the $(3:4,8^2)$ net from 120° leads to an energy gain compared with graphite, where the valence angles are 120°, The energy of the steric strain (E_{SS}) has been estimated[76] from the empirical formula $E_{SS} = 17.5\Delta\theta^2$ cal mol^{-1}, where $\Delta\theta$ is the deviation of the valence angles from the ideal value (120° or 109°28′16″ in the case of sp^2- or sp^3-hybridisation respectively). In estimating the relative stabilities of planar nets, account was also taken of the conjugation energy (E_{conj}) calculated in terms of the Hückel approximation.

Among the three-dimensional nets considered by Balaban et al.,[76] the net whose fragment is illustrated in Fig. 1*e* is of greatest interest. It is described in terms of truncated octahedra and the valence angles (90° and 120°) differ fairly appreciably from the tetrahedral values (the steric strain energy is 12 kcal mol^{-1}). The relative stability of this system was determined in relation to diamond (cubic) and the relative stabilities of graphite and diamond were estimated from the difference between the enthalpies of formation. The energies of the other (planar) forms shown in Fig. 1 were estimated in the way described above and were assumed to be $E_{SS} + E_{conj}$. This analysis resulted in the following stability series (in kcal mol^{-1}): graphite (0.0), cubic diamond (0.5), hexagonal diamond (3.0), system (*c*) (7.5), system (*e*) (12.0), and system (*b*) (17.0). A higher energy corresponds to the other nets considered in the above study.[76]

It is seen from the above analysis that the estimates obtained[76] are extremely approximate. In particular, the authors[76] in essence restricted their treatment to a purely topological approximation and did not attempt to estimate the bond lengths in the carbon structures which they considered. Apparently, the assumption of the planar character of the systems and in particular of the net made up of four- and eight-membered rings is insufficiently justified. For example, it is known that the eight-membered carbon ring in cyclo-octatetraene and its octamethyl derivatives is non-planar; a doubt therefore arises about the reality of system (b) which can hardly be planar.

Planar regular nets are the limiting case of finite nets which can be produced on a sphere with a sufficiently large radius. In this case a convex polyhedron can be associated with each such net. The possibility of the existence and methods of synthesis of some of the hydrocarbon systems whose carbon atoms are located at the vertices of the simplest polyhedra (the cube, the trihedral prism, the tetrahedron, and the dodecahedron) has been discussed in a number of studies.[77–82]

The possibility of the occurrence of the analogous unsaturated purely carbon systems—molecules whose atoms are located at the vertices of polygons or polyhedra has been considered in a number of studies.[83–89] Certain results obtained for small carbon clusters, including planar clusters, are of interest in this connection. For example, the potential energy surface for the C_3 triatomic molecule has been investigated[83] by the non-empirical LCAO-MO method. It was established that a linear configuration is most stable

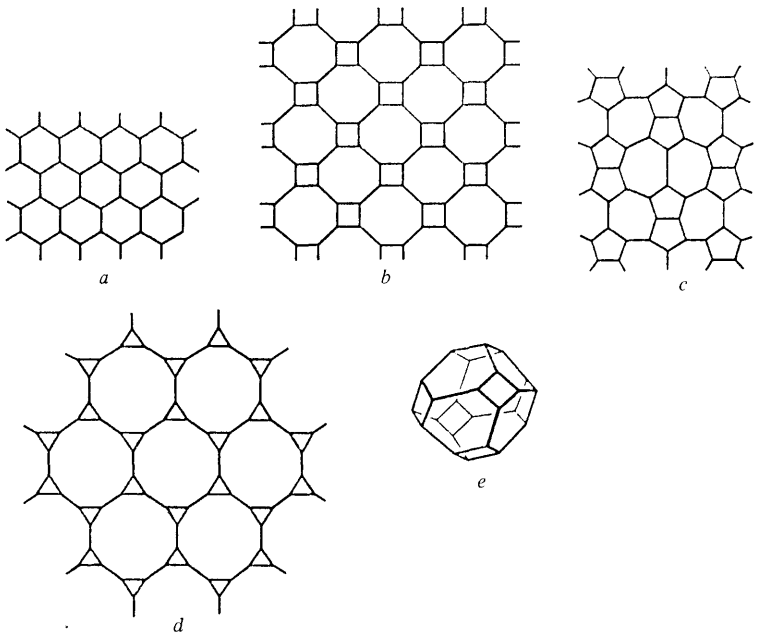


Figure 1. Some of the carbon systems considered by Balaban et al.[76]: *a*) $(3:6^3)$ graphite layer; *b*) $(3:4,8^2)$ system; *c*) (3:5,7) system; *d*) $(3:3,12^2)$ system; *e*) fragment of three-dimensional net.

for this molecule. Furthermore, a local minimum, corresponding to a trigonal configuration of the nuclei in the form of an isosceles triangle, was noted on the potential energy surface. The molecule has a triplet ground state.

A recent calculation for the C_4 cluster led to an unexpected result. It was found that the cyclic system in the form of a rhombus is energetically more favourable than the linear system.[84] The relative stabilities of various symmetrical configurations of clusters having the composition C_p ($p = 3-7$) have been discussed[85] within the framework of the semi-empirical MINDO/2 approximation. In particular, it was established that, for each of the C_3-C_7 clusters, there exist at least two isomers and that the absolute energy minimum corresponds to a non-linear configuration. For example, in the case of C_4 the most stable configuration is the rhombus (D_{2h} symmetry), which is consistent with the conclusions reached[84] by a non-empirical method. A distorted octahedral configuration obtains for C_6. In the case of C_4 a linear configuration proved to be unstable, but for other clusters (C_5, C_6 and C_7) local minima on the potential energy surface correspond to linear configurations. The relative stabilities of small carbon clusters have also been discussed by Beran et al.[86]

The electronic structures and relative stabilities of the carbopolyhedra with a large number of carbon atoms have been investigated.[87-89] The authors of these studies carried out calculations by various quantum-chemical methods for the carbododecahedron (C_{20}), the carbo-*s*-octahedron (C_{24}), which is a polyhedral fragment of the three-dimensional net (*e*) (Fig. 1), and carbo-*s*-eicosahedron (C_{60}) (Fig. 2).

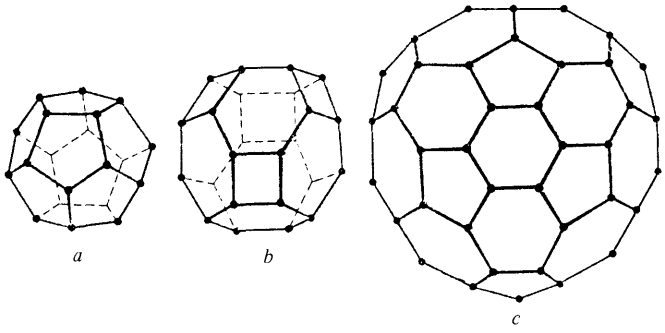


Figure 2. Carbopolyhedra: *a*) carbododecahedron; *b*) carbo-*s*-octahedron; *c*) carbo-*s*-eicosahedron.[87]

In the simplest case an approximation analogous to the Hückel approximation for planar unsaturated conjugated systems, which has been called[87-89] the ρ-approximation, was used. It was assumed that the σ-skeleton of the carbopolyhedra is made up of two-centre two-electron banana bonds in which the 2*s* and 2*p* orbitals of the carbon atoms participate. The remaining *p* orbitals are directed along the radius of the sphere described and the electrons associated with these orbitals are involved in the formation of the ρ-system on the sphere analogous to the π-system in the limiting case of the sphere—the plane.

The calculations performed in terms of the ρ-approximation[83] showed that the ρ-electron shell of the carbododecahedron is not closed (in the highest quadruply degenerate level there are two electrons), while the carbo-*s*-octahedron and the carbo-*s*-eicosahedron have a closed electron shell. The calculations performed with the aid of the EHM confirmed the conclusion concerning the character of the electron shells of the ground states of the carbododecahedron, the carbo-*s*-octahedron, and the carbo-*s*-eicosahedron. By varying the C–C bond lengths in C_{20}, C_{24}, and C_{60} while retaining the ideal symmetry for these systems, an equivalent value close to the length of a single bond was attained. In the case of the C_{20} system the above calculation shows that such a molecule, if it exists, should have the form of a distorted dodecahedron. Naturally, the symmetry of the carbododecahedron can be reduced by replacing two carbon atoms by boron atoms and by reducing thereby the total number of ρ-electrons by two. Such systems have a closed electron shell (EHM, ρ-approximation) and it is believed[87-89] that no obstacle to the possibility of their existence has so far been found.

The results described above have been confirmed by calculations carried out by the CNDO-2 method.[88,89]

We shall now proceed to the description of certain connected three-dimensional infinite regular nets, which can be achieved in three-dimensional space in such a way that the valence angles are equal to or close to the classical values. Apparently, one of the first studies on these lines[90] was published as early as 1946; its authors describe the structure of carbon made up of six-membered rings notated relative to one another. A net formed in three-dimensional space as a result of regular cross-links between the carbon skeletons of *o*-tetraphenylene, whose molecules are non-planar, corresponds to this crystalline modification of carbon. A net of this type has been used[91] to construct one of the possible models of amorphous carbon.

In relation to structural problems of crystal chemistry and crystallography, three-dimensional nets have been investigated systematically by Wells, who described a number of three-dimensional nets, suitable for the understanding of the topology of crystals with a complex structure, in a series of articles[92-103] about the geometrical principles of crystal chemistry, which were summarised in a monograph.[104]

In principle, any three-dimensional nets, including those with a regular structure, can be readily obtained with the aid of the operations involving the addition of new vertices or edges, for example, to a graph consisting of an infinite number of unconnected linear graphs. The problem consists in selecting those graphs which can be realised in the form satisfying the requirements formulated above.

A natural method of obtaining some of these nets (homogeneous graphs of degree 3), in which the valence angles, equal to 120°, are combined with a non-planar structure, has been described;[105,106] this is a type of coordination structure, as in diamond.

We may note that the planar layer of graphite can be regarded as a result of the formation of chemical bonds, i.e. regular cross links between zig-zag chains made up of carbon atoms located in a single plane. The valence angles are assumed to be 120° and each chain has two neighbouring chains. One can form analogously a chain made up of carbon atoms and having an *n*th order screw symmetry axis, in which the angles between the bonds along the chain are 120°, by distributing the carbon atoms along the edges of a regular straight *n*-hedral prism ($3 \leq n \leq 6$). Having arranged such prisms parallel to the *z* axis in such a way that each has *n* neighbours (Fig. 3), it is possible to form a system of cross links between the carbon chains which is periodic along the *z* axis. The periodic arrangement of the chains in space leads in this case to the formation of a crystal structure.

In fact, if it is assumed that the atomic orbitals are sp^2-hybridised, then the symmetry axis of the third hybrid orbital lies in a horizontal plane. Having arranged the set of chain macromolecules with parallel axes in space in a regular manner in such a way that in the direction of the horizontal hybrid atomic orbital (AO) of each atom there is an atom of a neighbouring chain (also having a hybrid atomic orbital directly at right angles to the z axis), it is possible to obtain a crystal structure in which each atom has three neighbours (two in its own chain and one in a neighbouring chain) and the valence angles are 120°. (When there is physical interaction between the atoms, there is a possibility of a distortion of the valence angles in certain structures.)

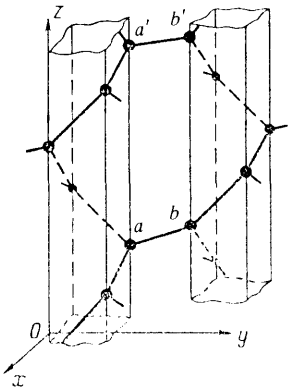


Figure 3. The principle of the construction of three-dimensional nets: the cross links between two adjacent chain systems having the 4_1 symmetry axis; the sections ab and $a'b'$ are parallel to the $z = 0$ plane.

Since fifth order [five-fold?] symmetry axes are impossible in crystals, it follows that $n \neq 5$. When $n = 6$, the chain degenerates into a planar regular hexagon and the cross-linking of such hexagons leads to the formation of a planar graphite layer. There remain two possible versions: with $n = 3$ and $n = 4$. When $n = 3$, the angles between the bonds along the chain are 120°, provided that the selected length of the side of the base of the trihedral prism is $r_1\sqrt{3}$ and the pitch of the helical chain (i.e. the difference between the z coordinates of the neighbouring atoms) is $r_1\sqrt{2/3}$, where r_1 is the distance between the neighbouring atoms along the chain. The distance r_2 between the nearest atoms of neighbouring chains is not related to r_1 and the choice of r_2 does not influence the symmetry of the crystal structure when $n = 3$. When $n = 4$, the valence angles are 120° when the side of the base of the tetrahedral prism and the pitch of the helical chain are $r_1\sqrt{2}$, where r_1 is also the distance between the neighbouring atoms along the chain.

Since the chains can have different chiralities, then for a given n there is a possibility of different versions of cross links leading to the formation of crystal structures. If the chiralities of the cross-linked chains are identical, then for a given n there is a possibility of only one method of cross-linking in which each chain with an nth order [n-fold?] screw symmetry axis is surrounded by n chains with the same chirality. The structures formed by the cross-linking of chain macromolecules of the same chirality will be designated by $C_1(n_j)$, where n_j characterises the screw symmetry axis of the chain macromolecule. The symbol $C_2(n)$ designates the crystalline carbon structures in which each chain with an nth order [n-fold?] screw symmetry axis is surrounded by n chains of the opposite chirality. In this case there is also a possibility of only one version of cross-linking. All the remaining structures formed by the cross-linking of chains of different chirality will be designated by the symbol $C_3^i(n)$, where i is an additional index. In structures of this type there are chains which have neighbours of different chirality.

Some of the other methods of cross-linking chain macromolecules described above, which lead to the formation of the $C_1(n_j)$, $C_2(n)$, and $C_3^i(n)$ structures, are shown in Fig. 4. Evidently it is possible to construct an infinite set of structures of the type $C_3^i(n)$; however, in modifications of this type the unit cells would contain too large a number of atoms.

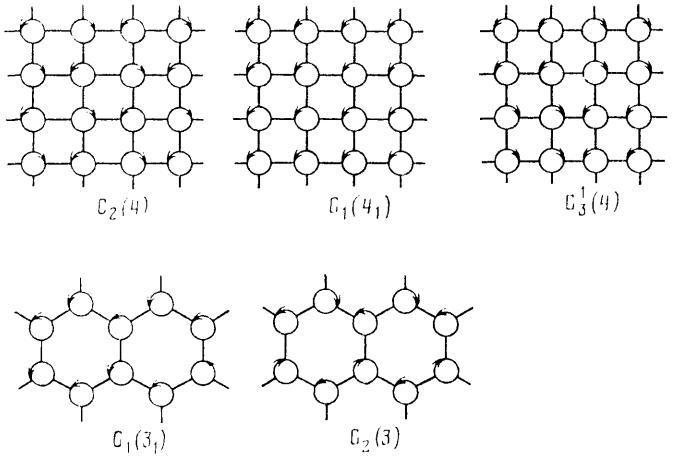


Figure 4. Classification of some of the three-dimensional crystalline modifications of carbon formed by cross links between chain macromolecules having symmetry screw axes of different orientations:[123] the orientations of the axes are indicated by arrows.

We shall consider in greater detail the crystal structures of certain modifications.

(a) *The $C_1(4_1)$ modification.* This modification is formed by the cross-linking of carbon chain molecules having 4_1 screw symmetry axes. Each of the chains has four neighbours of the same chirality. All the bonds are equivalent, so that one can assume that $r_1 = r_2 = r$. In the two directions perpendicular to one another and the 4_1 axis of each chain, there are helical chains of the same chirality as the initial chains.

The symmetry space group of the structure formed is $I4_132$ (see Bokii,[107] pp. 90, 104, No. 220). There is a body-centred cubic (BCC) Bravais lattice, in the unit cell there are eight carbon atoms, and the lattice parameter is $a = 2\sqrt{2}r$. The density of this modification ρ(g cm^{-3}) depends on the parameter r(Å) characterising the distance between the neighbouring carbon atoms: $\rho = 7.04/r^3$. For

example, $\rho = 2.46$ g cm^{-3} for $r = 1.42$ Å and $\rho = 1.93$ g cm^{-3} for $r = 1.54$ Å.

Each carbon atom in the $C_1(4_1)$ modification is located in one place with its neighbours, but the planes corresponding to sets of three terminal atoms in the C_6 fragments of the ethylene-like type intersect at an angle of 70°32′. By virtue of the total symmetry of the structure, when account is taken of the interaction between the atoms, significant distortions of the valence angles could not take place.

The enantiomorphic modification $C_1(4_3)$, formed by the cross-linking of chain carbon macromolecules having screw symmetry axes 4_3, has the $I4_332$ symmetry group. The scalar physical properties of the two enantiomers should be identical.

(b) *The $C_2(4)$ modification.* The structure of $C_2(4)$ and its projection on to the (001) plane are shown in Fig. 5. The $C_2(4)$ modification can be regarded as a result of the formation of regular cross links between chain carbon molecules having screw symmetry axes 4_1 and 4_3. Each chain has four neighbours of opposite chirality. All the valence angles can be chosen equal to 120°, provided that one disregards the possible distortions of the angles under the influence of interatomic interactions.

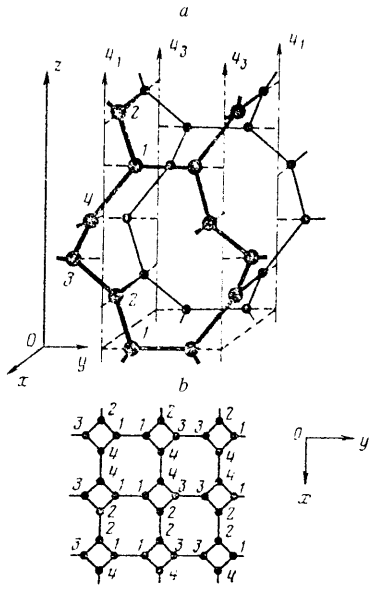


Figure 5. The crystal structure of the $C_2(4)$ modification:[112] *a*) structural fragment; *b*) view from above; identical numerals correspond to atoms whose *z* coordinates are equal or differ by amounts which are multiples of the period of translation along the *z* axis.

In contrast to the $C_1(4_1)$ modification, the bonds within the chain and between the chains are not equivalent. This is associated with the fact that the planes containing the carbon atom and the first layer around it are identical for the nearest atoms of neighbouring chains (the C_6 planar fragment), while non-planar C_6 fragments, with an angle of rotation of the corresponding planes of 70°32′ [the same as in $C_1(4_1)$], arise along the chain. The symmetry space group of this modification is $I\bar{4}m2$,[107] (pp. 80 and 96, No. 119). The Bravais lattice is hexagonal body-centred; the unit cell contains sixteen carbon atoms and the primitive cell contains eight carbon atoms. The unit cell parameters are $a = b = 2(r_1 + r_2)$ and $c = 2\sqrt{2}r_1$ The basis of the lattice consists of eight atoms; the volume of the unit cell is $v = 8\sqrt{2}r_1(r_1 + r_2)^2$. The density of this modification ρ depends on the two parameters r_1 and r_2: $\rho = 28.16/r_1 \cdot (r_1 + r_2)^2$. When $r_1 = 1.48$ Å and $r_2 = 1.34$ Å, we find $\rho = 2.39$ g cm^{-3}.

(c) *The $C_1(3)$ and $C_2(3)$ modifications.* The $C_1(3_1)$ modification and the enantiomorphic $C_1(3_2)$ modification have the symmetry space groups $P6_222$ and $P6_422$ respectively[107] (pp. 85 and 100, Nos. 183 and 184). The $C_1(3_1)$ modification, formed by the cross-linking of chain carbon macromolecules having symmetry screw axes 3_1, has a primitive hexagonal Bravais lattice containing six carbon atoms in the unit cell. The unit cell parameters are $\alpha = \beta = 90°$, $\gamma = 120°$, $a = b = (2r_1 + 3r_2)/\sqrt{3}$, and $c = r_1\sqrt{6}$, where r_1 is the distance between neighbouring atoms along the chains and r_2 is the distance between the nearest atoms in neighbouring chains.[106] The angles of rotation of the planes containing the atom and its immediate environment, corresponding to the transition to a neighbouring atom along the chain and to a neighbouring atom in a neighbouring chain, are 70°32′ and 38°56′ respectively. The density of the $C_1(3_1)$ modification with $r_1 = r_2 = r$ is defined by the expression $\rho = 6.76/r^3$; for $r = 1.48$ Å, we obtain $\rho = 2.08$ g cm^{-3}.

The $C_2(3)$ modification is made up by the cross-linking of chain carbon macromolecules having symmetry screw axes 3_1 or 3_2. Each chain has three neighbouring chains of opposite chirality. The Bravais chain is hexagonal and doubly body-centred, the unit cell contains eighteen carbon atoms, and the symmetry space group is $R\bar{3}m$,[107] (pp. 84 and 98, No. 166). The lattice parameters are $\alpha = \beta = 90°$, $\gamma = 120°$, $a = b = 2r_1 + 3r_2$, and $c = r_1\sqrt{6}$, where r_1 and r_2 have the same significance as for the $C_1(3_1)$ modification. The angles of rotation of the planes containing the atom and its first shell, corresponding to the transition from the atom to its neighbours along or between the chains, are 70°32′ and 0° respectively.

It is noteworthy that the projections of the structures described onto the (001) plane are of the same type as some of the planar carbon nets discussed[76] in connection with the assessment of the possibility of the existence of hypothetical planar carbon structures (Figs. 1 and 5).

We may also note that new crystal structures can be obtained from the crystalline modifications of carbon of the type $C_1(n_i)$, $C_2(n)$, and $C_3^i(n)$ by the formal replacement of the C–C bonds by the $-C\equiv C-$ fragments. Hybridisations of two kinds are formally obtained in crystalline modifications of carbon of this type: sp^2 and sp. According to Kasatochkin's classification,[53] these modifications refer to transitional forms of carbon.

As a result of the cross-linking of chain carbon macromolecules, it is possible to construct yet another homogeneous C_5 net. We shall consider a planar linear chain macromolecule consisting of an infinite number of carbon atoms and having the *trans*-configuration. Suppose that the lengths of all the bonds are identical and equal to r_1 and that all the valence angles are 120°. With the aid of the translational operation in a direction perpendicular to the molecular plane with a translation vector having a length $r_1\sqrt{3}$, we shall construct from the initial chain macromolecule an infinite family of its images, which are located in parallel equidistant planes. It follows from this method

of construction that the centres of all the bonds of the family of molecules obtained in this way are located in the same plane, which we shall designate by $\tilde{S}_0$. The set of all the macromolecules forms the layer S_0, consisting of chain macromolecules located in parallel planes and separated from one another by a distance $r_1\sqrt{3}$. We shall direct the z axis at right angles to the $\tilde{S}_0$ plane and the origin of coordinates will be placed in this plane. Then each atom of the $\tilde{S}_0$ layer has a z coordinate equal to either $r_1/4$ or $-r_1/4$.

We shall construct yet another layer S_1 of this kind. We shall rotate it relative to the initial layer by 90° and, having retained the previous orientation of the z axis, we shall place it above the S_0 layer at a distance r_2 in such a way that an atom of the S_1 layer with the z coordinate equal to $-r_1/4$ relative to the $\tilde{S}_1$ plane corresponds to each atom of the S_0 layer with a coordinate $r_1/4$ relative to the $\tilde{S}_0$ plane and both atoms are located on a single line perpendicular to the $\tilde{S}_0$ plane. It is easy to show that this procedure is feasible.

We construct analogously an S_{-1} layer and place it below the S_0 layer at a distance r_2. Continuing this process without limit, we obtain an infinite system of layers in which each even layer is rotated relative to the odd layer by 90° and an atom of the S_{n+1} layer with a relative z coordinate $-r_1/4$ corresponds to each atom in the S_n layer with a relative z coordinate $r_1/4$ and both atoms are located on a single straight line parallel to the z axis.

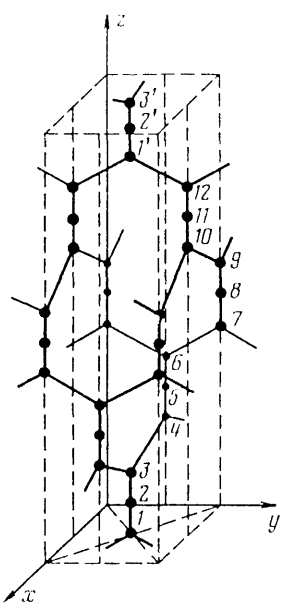
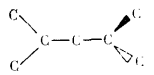


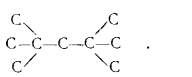
Figure 6. The crystal structure of allenocarbon; atoms *1–12* form the basis of the structure.

In the resulting structure all the valence angles are 120° and C_6 fragments of the ethylene type, with C_3 groups rotated relative to one another by 90°, are present. The C_8 net described with $r_2 = r_1$ coincides with one of the nets discussed in a monograph[104] (see also Hoffmann et al.[108]). It has a symmetry group $I4_1/amd$, a tetragonal lattice with the parameters $a = b = r_1\sqrt{3}$ and $c = r_1 + 4r_2$, contains eight atoms in the unit cell, and can be used to construct new structures. For example, we place along the sections connecting the atoms of two neighbouring layers an odd number (identical for all pairs of neighbouring atoms) n' of atoms. For $n' = 1$, the bond lengths can be chosen such that one obtains as a result a regular structure made up of fragments of the type



with two end groups rotated by 90° relative to one another. Such geometry is characteristic of compounds of the allene type[109] and we shall refer to this crystalline modification of carbon as allenocarbon (Fig. 6).

The same principle of construction has been applied by Mel'nichenko et al.[110] who used the diamond lattice for this purpose. If cubic or hexagonal diamond is represented as a structure made up of cross-linked carbon layers consisting of polycondensed carbon rings with a geometry close to that of the carbon skeleton of the cyclohexane ring, then several atoms can be placed at each cross link (the case of only one atom was considered by Mel'nichenko et al.[110]). As a result of this procedure, the layers move apart owing to the increase of the length of the interlayer cross links. However, in the case considered by Mel'nichenko et al.[110] somewhat unusual combinations of chemical bonds, made up of two tetracoordinate and one dicoordinate carbon atom, arise.



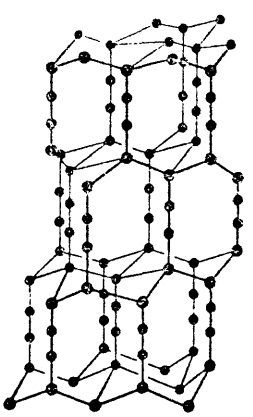
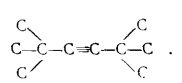


Figure 7. The crystal structure of poly-ynodiamond.[110]

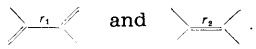
It would be more useful to distribute an odd number of atoms at the interlayer cross links, whereupon more natural structural elements of the poly-yne type would arise:



The modification obtained in this way on the basis of cubic diamond is illustrated in Fig. 7 (poly-ynodiamond).

A number of studies have been devoted to the relative stabilities of crystalline modifications of carbon. Data for the relative stabilities of planar hypothetic carbon systems of the mosaic type were presented above. It was noted that in these structures there are unusual combinations of bonds, which hinders the estimation of their lengths. On the other hand, in the $C_1(4_1)$ and $C_2(4)$ structures described in two investigations[105,106] the bond lengths can be estimated[111,112] using for this purpose the empirical relations between the internuclear distance separating chemically bound atoms and the bond type as well as data for the geometry of the carbon skeleton of hydrocarbon molecules, which are comparable to individual fragments of the crystalline modifications of carbon considered.

In structure $C_2(4)$ there are bonds of two types:



According to the data of Tatevskii and Spiridonov,[24] $r_1 = 1.48 \pm 0.02$ Å and $r_2 = 1.34 \pm 0.02$ Å. The structure $C_2(4)$ can also be described in terms of eight-membered rings (in the boat form). The geometry of these rings should be close to that of the carbon skeleton of the cyclooctatetraene molecule in which the C–C bond lengths alternate and amount to 1.462 and 1.334 Å.[113] In graphite the C–C bond length has inreased by approximately 0.02 Å compared with benzene. Similarly the C–C bond length in diamond has also increased by approximately 0.02 Å compared with cyclohexane (1.52 Å). These estimates show that in the $C_2(4)$ crystalline modification of carbon there should be bonds whose lengths are close to 1.48 and 1.35 Å.

In the $C_1(4_1)$ modification all the bonds are equivalent (in the geometrical sense). The inner bond of the C_6 fragment of the ethylene-like type, in terms of which it is possible to describe the $C_1(4_1)$ crystal structure, should be similar in its character to the C–C bond between the rings in biphenyl, i.e. its length should be close to 1.48 Å. Bearing in mind that the immediate environment of this bond persists on passing to the crystal, the C–C bond length in the $C_1(4_1)$ modification was assumed to be 1.48 Å.

Using the C–C bond lengths quoted above in the $C_1(4_1)$ and $C_2(4)$ modifications, the relative stabilities of these systems have been estimated[111,112] in relation to diamond, graphite, and two carbyne modifications: α- and β-carbyne. The relative stabilities were estimated in the following way: with the aid of three empirical relations between the bond energy and bond length or bond type:

A. From the Dewar–Schmeising formula:[114]

$$\varepsilon(r) = -\frac{1140.593}{r} + \frac{3252.755}{r^2} - \frac{1199.129}{r^3},$$

B. From the linear relation obtained on the basis of Popov and Kogan's data.[62]

C. From the dependence of the bond energy on the bond type according to Popov and Kogan's data.[62]

D. By the virial-statistical method.[115]

The bond energies in the crystalline modifications considered were calculated in the first three instances from the formula

$$E = \frac{1}{2}\sum_i n_i \varepsilon(r_i),$$

where the summation extends over all the bonds of the given atoms and n_i is the number of bonds of the given type per carbon atom.

We shall consider in greater detail the estimation of the bond energy of the crystal by the virial-statistical method, which is based on the representation of the energy of the ground state of the quantum system in the form of a functional of the electron density.[116] The electron density of the molecule (crystal) is represented approximately by the sum of the electron densities of the atoms, which were evaluated on the basis of the calculations for the atoms carried out by Clementi and co-workers.[117,118] Next it is assumed that the virial theorem holds and that the total energy can be calculated as half the potential energy.

The potential energy is calculated in terms of the approximation within the framework of the statistical theory taking into account the Coulombic, exchange, and correlation contributions.[115]

The Table presents the relative bond energies for graphite, diamond, $C_2(4)$, $C_1(4_1)$, α-carbyne, β-carbyne, and allenocarbon calculated by the four methods A, B, C, and D indicated above. It follows from the tabulated data that, for all the methods used in estimates, the $C_2(4)$ modifications should be more stable than the $C_1(4_1)$ modification and also more stable than the α- and β-forms of carbyne.

Interatomic distances and the calculated* bond energies E(C–C) for certain crystalline modifications of carbon.

Structure	r_1, Å	r_2, Å	$-E$(C–C), kcal mole^{-1}			
			A	B	C	D
Graphite	1.42	—	0.0	0.0	0.0	0.0
Diamond	1.54	—	0.3	1.0	0.9	1.5
$C_2(4)$	1.34	1.48	5.3	4.8	6.0	7.4
$C_2(4_1)$	1.48	—	14.4	14.6	23.3	32.5
β-Carbyne	1.28	—	27.0	23.1	20.9	33.6
α-Carbyne	1.38	1.20	31.8	25.6	24.0	32.8
Allenocarbon	1.31	1.51	18.4	16.4	9.1	8.0

*Methods of calculation: A) from the formula for $\varepsilon(r)$ quoted by Dewar and Schmeising;[114] B) from the formula for $\varepsilon(r)$ quoted by Popov and Kogan;[62] C) from the average bond energies;[62] D) by the method of the electron density functional.[115]

In conclusion of this Section, we shall mention a study[119] in which the relative stabilities of certain skeletal hydrocarbon oligoradicals are discussed in connection with the problem of the existence of three-dimensional carbon structures with sp^2 hybridisation of the carbon atoms.

2. The Nature of the Chemical Bonds and the Structure of the Band Spectra of Certain Hypothetical Crystalline Modifications of Carbon

It is known that diamond is a dielectric and that the width of the forbidden gap at 295 K is 5.49 eV for indirect transitions.[120] The width of the forbidden gap in the graphite spectrum is close to zero and graphite is a semi-metal. The resistivity of the graphite single crystals in the plane of the aromatic ring is smaller by several orders of magnitude than in the direction of the translational c axis. The electronic spectrum of graphite has been discussed in a number of studies[17,18,121,122] in which an extensive bibliography on graphite has also been given.

It is of interest to analyse the possible electrophysical properties of the hypothetical crystalline modifications of carbon which were discussed above. This problem has been discussed in a number of communications for modifications of the type $C_2(4)$, $C_1(4_1)$, $C_1(3_1)$, etc. We shall consider initially in greater detail the results of the study of the band spectra of the $C_1(4_1)$ and $C_2(4_1)$ structures. In estimating the band spectra of these modifications, the authors[123-125] used a model according to which the $2p$ electrons (one from each atom) located in the $2p$ orbitals (the symmetry axis of each orbital is perpendicular to the plane passing through the corresponding atoms and its three nearest neighbours) and moves in the field of the σ-skeleton of the system; the remaining three valence electrons from each atom participate in the establishment of this field. This mathematical model is analogous to that employed in the calculations for non-planar conjugated systems of the type of biphenyl in terms of the π-electron approximation. The total energy of the crystal in this model depends only on the crystal orbitals made up of the $2p$ orbitals which are not involved in the formation of the σ-skeleton. Each crystal orbital is referred to a definite wave vector **k** and is sought in the form of linear combinations of Bloch functions.

In the version of this method without adjustment for self-consistency the absolute values of the diagonal elements of the Hamiltonian were assumed to be equal to the valence ionisation potential I_p of the carbon atom. The non-diagonal elements of the Hamiltonian $H\mu\nu$ were estimated from the Wolfsberg–Helmholtz formula $H\mu\nu = -1.75\, I_p S\mu\nu$, where $S_{\mu\nu}$ is the overlap integral of $2p$ atomic orbitals of the neighbouring carbon atoms. The interaction between non-neighbouring atoms was disregarded.

For the main symmetrical directions in the first Brillouin band of the $C_1(4_1)$ modification, analytical formulae have been obtained whereby one can find the one-electron energy levels as a function of the wave vector **k**. The dispersion laws for the main symmetrical directions in the first Brillouin band corresponding to a bond length of 1.48 Å are presented in Fig. 8. The valence ionisation potential I_p was assumed to be 11.4 eV. Fig. 8 shows that the $C_1(4_1)$ modification (within the framework of the model adopted) has a band spectrum characteristic of metals. The Fermi energy is $-I_p$.

Calculation of the band spectrum of the $C_1(4_1)$ modification within the framework of the method of crystal orbitals adjusted for self-consistency in terms of the Pariser–Parr–Pople (PPP) approximation (taking into account the two-electron interaction integral γ_0 at only one centre) did not alter the conclusion that the spectrum of the $C_1(4_1)$ modification has a metallic character in the case of the restricted Hartree–Fock method; the Fermi energy increases by $\gamma_0/2$ (approximately 5 eV) when account is taken of the inter-electron interaction.

In order to estimate the influence of the non-orthogonality of the $2p$ atomic orbitals with respect to the orbitals of the σ-skeleton on the band spectrum, the one-electron energies of the $C_1(4_1)$ modification were calculated[126] in terms of the valence approximation (at the centre of the first Brillouin band). The calculation showed that the model adopted reproduces fairly correctly the qualitative features of the spectrum, because, in terms of the valence approximation, the $C_1(4_1)$ modification also has a spectrum with a metallic character.

Within the framework of the same model, the band spectrum of the $C_2(4)$ modification has been estimated.[125] The calculation was performed using bond lengths of 1.48 and 1.34 Å for bonds along and between the chains respectively. In the spectrum of the $C_2(4)$ modification there is a forbidden gap and the maximum one-electron energy in the valence band and the minimum energy in the conductivity band are attained at the centre of the first Brillouin band, i.e. when $k = 0$. It follows from the calculation that the $C_2(4)$ modification should have semiconducting properties. The width of the forbidden gap in the spectrum is 2.2 eV for the parameters selected by Nikerov et al.[124]

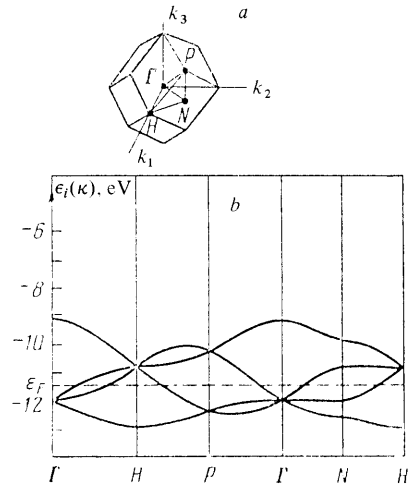


Figure 8. The band structure of the spectrum of the $C_1(4_1)$ crystalline modification of carbon: *a*) first Brillouin band (Γ—centre of band, *N*—centre of face, *H* and *P*—vertices); *b*) dependence of the one-electron energy levels $\varepsilon_i(\mathbf{k})$ on the wave vector $\mathbf{k} = (k_1, k_2, k_3)$ along the ΓH, HP, $P\Gamma$, ΓN, and NH directions; the dashed line indicates the position of the Fermi level ε_F.[123]

The spectrum of the crystalline modification constructed on the basis of the C_8 net and described above has been discussed.[108] Although in this net all the valence angles are 120°, the conjugation between the chains in different layers breaks down completely, in contrast to the $C_2(4)$ and $C_1(4_1)$ modifications considered above. The authors[108] estimated the C–C bond length for the polyene chain as 1.44 Å and obtained 2.494 Å for the distance between the polyene chains. With these values of the geometrical parameters, this modification has a density of 3 g cm^{-3}, i.e. intermediate between those of graphite and diamond. In terms of the EHM approximation, the modification has an energy spectrum of the metallic type with fairly broad bands and the energy of the Fermi level is approximately −10 eV (one should bear in mind that, in terms of the EHM approximation, this value is usually too low by 3–5 eV). Allowance for the possible alternation of the bond lengths in the polyene fragment does not introduce qualitative changes into the character of the spectrum, in contrast to the one-dimensional case.

Calculations for model macromolecular hydrocarbon systems, carried out in order to elucidate the factors influencing the band width in the three-dimensional structure, showed that the influence of the interchain interaction should be fairly strong. The authors[108] note that the Mulliken bond orders, found for the atoms located in adjacent polyene chains of the three-dimensional structure, proved to be positive, which

showed that there is an overall predominance of the bonding interaction between the chains.

3. Certain Considerations Concerning the Possibility of the Existence of New Crystalline Modifications of Carbon

In this Section of the review we shall attempt to draw certain structural analogies between the known crystalline modifications of carbon and hydrocarbons. Such analogies can be used as additional evidence in support of the possibility of the existence of new crystalline modifications of carbon.

Different hydrocarbon systems correspond to diamond and graphite, the structures of their carbon skeletons being close to the local structures of diamond and graphite. For graphite, these are benzene, naphthalene and other polyacene systems, coronene, and polycondensed aromatic hydrocarbons, while for diamond these are cyclohexane, adamantane, etc.

As mentioned above, the $C_2(4)$ structure can be described in terms of eight-membered rings characteristic of cyclo-octatetraene. The structures of cyclo-octatetraene and its octamethyl and octaphenyl derivatives have been thoroughly investigated. In all three molecules the ring has the boat conformation. The average length of a single bond in cyclo-octatetraene (1.462 Å) increases somewhat on passing to the methyl and phenyl derivatives (1.487 and 1.493 Å respectively). The length of the double bond is in the range 1.33–1.35 Å.

The synthesis of octalene—an unsaturated hydrocarbon formed by the condensation of two eight-membered rings—has been reported.[127] An interesting class of unsaturated hydrocarbons—cyclophane compounds—is known.[128] Some of these "multidecker" systems consist of two or more unsaturated six-membered rings linked by $-C_2H_2-$ bridging groups. The molecules have an interesting geometry: the planarity of the rings breaks down, the valence angles deviate from the standard values, and the system becomes strained.

If the six-membered fragments are now "replaced" by eight-membered fragments, no significant distortions of the valence angles should occur. Hypothetical systems of the type $C_{24}H_{16}$ with valence angles close to the ideal values arise. On the other hand, the carbon skeleton of the $C_{24}H_{16}$ molecule constitutes a polyhedral fragment of the $C_2(4)$ modification (Fig. 5). The synthesis of the molecule described above, which is itself of interest, might serve as additional proof of the possible existence of the $C_2(4)$ crystalline modification of carbon.

Next the crystalline modifications of carbon formed by tricoordinate carbon atoms can be described in terms of hexa-atomic fragments of the ethylene type:



In order to assess the possibility of the formation of carbon fragments of the ethylene type with rotated C_3 groups, calculations have been made[126] of the energy of the C_6 clusters of the form described above (the valence angles were assumed to be 120°) by the CNDO/2 and INDO methods as a function of the angle of rotation (the C–C bond lengths were assumed to be equal and were optimised). It was established[126] that the total energy, expressed as a function of ψ, is a minimum for $\psi = 90°$ and a maximum for $\psi = 0°$. This property of the energy is determined in the first place by the behaviour of the interaction energy of the nuclei, which is a minimum for $\psi = 90°$. On the other hand, the interelectron interaction energy is a maximum for $\psi = 90°$, but its increase is compensated by the energy of repulsion of nuclei, which decreases fairly rapidly. The equilibrium C–C bond length is close to 1.33 Å.

This calculation permits the conclusion that in the gas phase there is a possibility of the formation of C_6 clusters of the type considered; this supports the possibility of the existence in polymeric carbon of C_6 structural fragments with end groups rotated relative to one another. This possibility is also indicated by the non-planar structure of the biphenyl molecule in the gas phase: the angle of the relative rotation of the six-membered rings is approximately 42°.[129]

Thus one may conclude that diamond, graphite, and carbyne do not exhaust the possible crystalline structures which do not conflict with the ideas established at the present time concerning the ability of carbon atoms to participate in the formation of chemical bonds. Problems associated with a more detailed description of the geometry, energy relations, and spectroscopic and other physico-chemical properties of the hypothetical structures naturally remain open. All these problems can be solved, in principle, for each specific instance.

In particular, it follows from the above analysis that under normal conditions a metastable form of carbon with metallic properties can exist. It may be that some of the structures discussed above are realised among the wide variety of the existing crystalline modifications of carbon whose structure has not been established.

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Nesmeyanov Institute of Organoelemental Compounds,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 1125-1151 (1984)

The Preparation of Labelled Organic Compounds by Treatment with Atomic Tritium

A.V.Shishkov, L.A.Neiman, and V.S.Smolyakov

The methods for the atomisation of gaseous tritium by thermal dissociation or under the influence of a high-frequency discharge, the reactions of atomic tritium, and its use for the preparation of labelled organic compounds are considered. Special attention is devoted to labelled biologically active compounds.
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I. INTRODUCTION

The use of isotopic methods has exerted an extremely significant influence on the development of a whole series of branches of science and technology and in chemistry, biology, and fields located at the junction between these two sciences, namely biochemistry, molecular biology, and bio-organic chemistry, the application of isotopes has undoubtedly proved particularly fruitful.

Although compounds labelled by isotopes of organogenic elements are used in the isotopic method in both organic chemistry and in biological disciplines. the requirements which they must meet differ greatly in most cases. In the study of the mechanisms of organic reactions, one is interested primarily in the position of the label in the molecules of the starting materials and products; on the other hand, the concentrations of these substances are as a rule fairly large. For this reason, one uses here specifically labelled compounds (i.e. compounds labelled at a particular atom) whose molar radioactivity is not too great.

In biochemistry, molecular biology, and bio-organic chemistry, the isotopic method has come to be most widely used as a procedure for qualitative and quantitative analysis, its high sensitivity being particularly important because it makes it possible to determine reliably substances at concentrations close to those at which their biological activity is manifested. Since the sensitivity of the method is unambiguously related to the molar radioactivity (a) of the labelled compound, a tendency has clearly arisen recently towards using tritium-containing compounds instead of their analogues labelled with carbon-14 (when a single T atom is introduced into a molecule, $a \cong 30$ Ci mmol^{-1} compared with 0.064 Ci mmol^{-1} for ^{14}C) and also towards the use, together with compounds labelled specifically with tritium, also of multiply labelled compounds (labelled in more than one position in the molecule), of non-specifically labelled compounds (i.e. those in which the exact distribution of T atoms in the molecule is unknown), and generally labelled compounds (those labelled in all possible positions). All these features make it possible to increase a to 100–200 (and sometimes more (Ci mmol^{-1}. Using certain other radioactive isotopes of organogenic elements (^{32}P, ^{33}P, ^{35}S, and ^{125}I), it is possible to achieve even higher values of a; however, in contrast to tritium and ^{14}C, these isotopes are not universal for organic compounds, which naturally narrows the region of their applicability.

Other advantages of tritium over ^{14}C are its weaker β-emission, the possibility of introducing the tritium label by exchange methods, and also the much lower cost of tritium-labelled compounds.

Thus the importance of tritium-containing compounds as research tools is particularly great in biology and related disciplines and the development of methods for the introduction of the tritium label into organic compounds (in the first place into complex molecules of biopolymers) is required very urgently. In order to obtain compounds labelled with tritium, chemical (synthesis), biological (biosynthesis, and enzymic reactions), and exchange (isotope exchange) methods are used.[1,2] However, one should bear in mind that, for a whole series of complex organic compounds, chemical synthesis has so far been either not described at all or its achievement in the isotopically labelled version is virtually impossible. Biosynthesis is also by no means possible in all cases and frequently it does not allow the attainment of the required values of a and involves considerable difficulties in the isolation and purification of the products.

The important advantages of exchange methods are their universality, the presence of only one stage in the process ("high speed"), and the fact that they do not require the presence of the corresponding precursors and permit the introduction of tritium directly into the "finished" molecule. The exchange methods can be divided into catalytic (see Neiman's review[3]) and methods which can be called physical. The latter are understood to involve the substitution of hydrogen by tritium as a result of the interaction of organic compounds with tritium ions or atoms possessing an excess energy (hot tritium atoms, atomic beams, activation of gaseous tritium by its intrinsic β-emission or external factors—ultraviolet light, high-voltage electric discharge, high-frequency microwave discharge, and thermal dissociation).

In all probability the first method of this kind is that of Wilzbach,[4] which consists of the maintenance of the given substance in an atmosphere of gaseous tritium. The exposures required for the appreciable incorporation of the label were fairly long: ranging from several days to months. The Wilzbach method is universal, but its application entails vigorous decomposition reactions of the test substance, the formation of a large amount of labelled side products, and a low coefficient of utilisation of tritium. In subsequent years a whole series of improved versions of the Wilzbach method were proposed, but fundamental improvements—a decrease of

the degree of decomposition of the test substance and an increase of α—were achieved only using activated tritium atoms as the main reactive species.

The present review is devoted precisely to these methods for the activation of gaseous tritium—the thermal dissociation method and the discharge method (particularly the microwave discharge in the high-frequency and ultrahigh frequency ranges), which will be designated below as TAM (the thermal activation method) and HFAM (the high-frequency activation method). Both procedures have been investigated very vigorously and improved during recent years, but the data referring to them are being surveyed for the first time. Their advantages include true rapidity (the duration of exposure is 0.25–60 min), universality, and the possibility in many instances (this applies particularly to the TAM) to reduce the consumption of tritium in a single experiment to several tens of millicuries. The latter factor is extremely important, since it permits experiments in radioisotope laboratories of class III where special protective equipment is not required.

On the other hand, the trend which has arisen in the employment of radioisotopic methods in biological disciplines can be formulated thus: increasing numbers of a wide variety of labelled compounds with an increasingly complex structure are needed; it is required to reduce their amounts as much as possible but to maintain at the same time a high molar radioactivity. For this reason, the commercial manufacture of such compounds, which involves the development of individual methods of purification, storage, and analysis, has become increasingly complex and expensive. The most attractive solution to this problem evidently involves the creation of a cheap, reliable, universal, and rapid laboratory method for the introduction of the label†; we believe that the HFAM and particularly the TAM are suitable candidates as laboratory methods of this kind.

The mechanisms of the processes leading to the incorporation of the label in the compound on treatment with atomic tritium and the methodological problems associated with the practical application of the TAM and the HFAM are examined below. The Wilzbach method and its modifications are not included in this review, because, firstly, they have already been considered in detail (see, for example, the relevant reviews[1,5]) and, secondly, in most cases the involvement of tritium atoms in these reactions has not been reliably demonstrated. However, these procedures as well as the results of experiments with atomic beams[6] and data on the chemistry of hot tritium atoms[1,7] will be employed so far as it is necessary for the comparison of the results and the analysis of the theoretical principles of the TAM and the HFAM.

II. THE PREPARATION OF ATOMIC TRITIUM BY THE HIGH-FREQUENCY ACTIVATION METHOD

The fact that the microwave discharge plasma contains high concentrations of atomic hydrogen in various excited and ionised states has been known for a fairly long time and this is the basis for the employment of discharges in the high-frequency and ultrahigh-frequency ranges as sources of hydrogen atoms and ions in the acceleration technology and as sources of resonance ultraviolet radiation.

The first report[8] of the use of a high-frequency discharge for the preparation of labelled compounds apparently appeared in 1960. It was shown later[9,10] that the introduction of the label is due to the tritium–hydrogen exchange occurring with participation of tritium atoms. Best results are achieved when the discharge is initiated in hydrogen diluted with helium and not in pure hydrogen: the intensity of the molecular bands in the emission spectrum diminishes and the intensity of the atomic hydogen line at 121.6 nm increases and at a frequency of 40 MHz the line becomes the only one present in the spectrum of a mixture containing 99% of helium.[11] The introduction of metallic electrodes into the discharge contaminates the plasma as a consequence of the atomisation of the material of the electrodes and in addition there is an appreciable reduction of the yield of hydrogen atoms owing to their recombination on metallic surfaces. Sources with an electrodeless discharge, i.e. apparatus in which the discharge tube containing the working gas (tritium or its mixture with an inert gas) is placed in a high-frequency field generated by external electrodes, are free from this disadvantage.

Sources of two types are usually employed—with initiation of the discharge in the region of high frequencies (tens and hundreds of MHz) and ultrahigh frequencies (thousands of MHz). The two discharges differ both as regards the conditions for the existence of a stable plasma and the apparatus used. In the high-frequency range the discharge is initiated at relatively low pressures (10^{-2}–10^{-3} mmHg) and its characteristics depend significantly on the frequency of the gases employed and the entire apparatus, particularly the components located in the discharge zone; the intensity of the resulting atomic beam in a high-frequency discharge is usually lower by two–three orders of magnitude than in the ultrahigh-frequency range. A discharge at a frequency of 2450 MHz is initiated at a pressure of the working gas of 1–5 mmHg and the beam obtained has an intensity of $\sim 10^{14}$–10^{15} atoms cm^{-2} s^{-1}; the characteristics of the discharge depend less on the presence of impurities, but the design of the apparatus is in this case more complex. Fig. 1 illustrates schematically the apparatus for the preparation of hydrogen (tritium) atoms with the excitation source in the region of 40 MHz. It has been shown on apparatus of this kind[12] that the yield of the principal labelled product—the parent compound—is almost independent (for an infinitely thick target) of the energy of the incident species in the range 0.5–5.0 keV.

The introduction of the label is possible not only by means of a neutral atomic beam but also with the aid of tritium ions T^+. Here charge transfer takes place in the first stage: $T^+ + RH \rightarrow T^* + RH^*$ (the asterisk denotes the excited state) and the label incorporation process itself takes place with participation of a neutral atom. The formation of excited states is due to the fact that the charge transfer conditions differ from resonance conditions. Processes leading to the thermalisation of a fast ion and to charge transfer are accompanied by the excitation of the molecules of the medium, whose character resembles that occurring under the influence of radiation. This can lead to the degradation of the test substance, which is not observed in the case of neutral species, as demonstrated fairly convincingly by comparing the effects on the target of beams of helium atoms and ions with the same kinetic energies.[12] For the preparation of labelled compounds, the apparatus can be significantly simplified:[13] instead of a system of beam focussing electrodes and the charge transfer chamber, one uses a narrow withdrawing channel at the Earth's potential, which is located at the end-face of the source and is shielded from the effects

†When the label is to be introduced into complex biological substances, it is important to ensure direct contact between the user and an investigator familiar with the procedures involved in experiments with the given specific compounds; this can be readily achieved if the labelled preparation is obtained in the laboratory where it is to be employed.

of the plasma. The form of the withdrawing electrode-channel is chosen empirically so as to ensure the best focussing of the beam; charge transfer involving atomic ions is achieved mainly in the source itself and in the channel of the electrode. The target is located at a short distance from the source and the intensity of the beam of particles is fairly high.

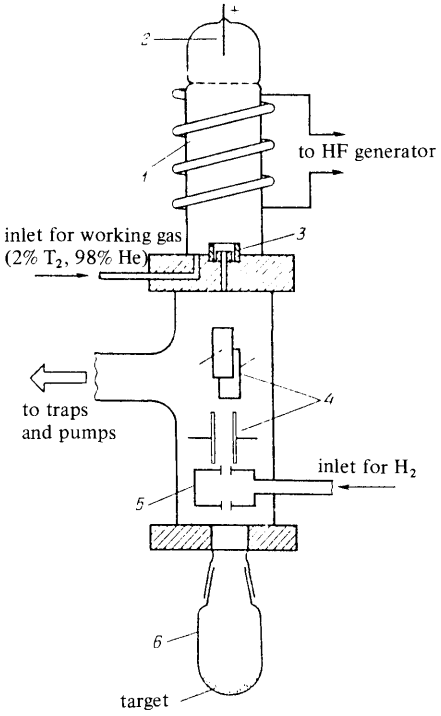


Figure 1. Apparatus for the preparation of fast tritium atoms by charge transfer involving atomic ions: 1) ion source with an electrodeless ring discharge (40 MHz); 2) accelerating electrode; 3) focussing electrode; 4) deflecting plates; 5) charge transfer chamber; 6) removable vessel for the target.

A source of atomic hydrogen with ultrahigh-frequency excitation has been used to synthesise tritium-labelled preparations.[10] The high pressure in the system and the large distance between the source and the target resulted in a low energy of the interacting atoms, which corresponded to the temperature of the walls. The apparatus is shown schematically in Fig. 2: a standard 2450 MHz generator and a standard microwave cell were used. The apparatus was connected to a pump which ensured continuous circulation of the working gas through the discharge and target zones at a controlled rate. The power evolved in the discharge is fairly high and the discharge is accompanied by an intense emission in the visible and ultraviolet regions, which may cause the photochemical decomposition of the test substance; for the protection from the latter, the target was placed outside the field of "vision" of the source. In apparatus with a high-frequency discharge, the intensity of the emission in the visible region is low and in addition only a small fraction of the emission can reach the target after passing through the narrow aperture (1–2 mm in diameter) of the withdrawing electrode. As already mentioned, in order to ensure the stability of an ultrahigh-frequency discharge, a fairly high gas pressure (~4 mmHg) is necessary, which corresponds to 1 Ci of tritium for apparatus whose volume is 500 cm^3.[10] An advantage of the high-frequency discharge is the low pressure (10^{-2}–10^{-3} mmHg), which corresponds to the consumption of 1–10 mc for the same volume. The high coefficient of the incorporation of tritium in the target makes it possible to employ the apparatus with a high-frequency discharge under conditions where the working gas flows through the discharge zone and beyond the pump it is sufficient to place a device for the oxidation of tritium and a trap. On the other hand, in apparatus with a UHF discharge, it is necessary to employ repeated gas circulation as a consequence of the low coefficient of the incorporation of tritium in the target due to the low energy of the atoms, which requires the inclusion of an additional pump and a more effective geometry of the apparatus. Furthermore, as the reaction proceeds, the working gas is enriched in protium.

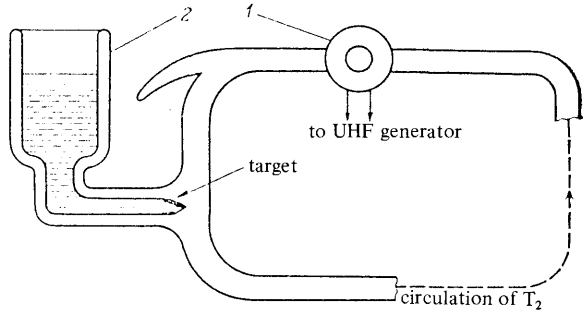


Figure 2. Schematic illustration of the apparatus for the introduction of the label with the aid of tritium atoms generated in an ultrahigh-frequency discharge (2450 MHz): 1) microwave cell; 2) trap with liquid nitrogen for the cooling of the target. The pump for the circulation of tritium and the system of pressure sensors are not shown in the diagram.

As regards the influence of various parameters on a, it has been found that the value of a for the labelled product increases with decrease of the thickness of the target or with increase of the duration of exposure to 5 min and is independent of the power of the discharge.[10] An increase of the distance from the source to the target reduces the yield of the labelled product. Low energies of tritium atoms are responsible for the dependence of the degree of incorporation of the label on the target temperature—on passing from 77 to 300 K, the activity a increases by a factor of ~5, but the degree of degradation of the test substance increases at the same time.

III. THE PREPARATION OF TRITIUM ATOMS BY THE THERMAL DISSOCIATION OF T_2

High temperatures in the range ~2000–3000 K are necessary in order to dissociate molecular hydrogen into atoms at an appreciable rate. On the other hand, the so-called furnace

sources employed in the molecular beam technique make it possible to heat the gas only to several hundreds of degrees and are naturally unsuitable for the preparation of atomic hydrogen. A novel and extremely simple technical solution has been found on the basis of the phenomenon of the catalytic dissociation of hydrogen on heated metallic filaments, which had been observed a long time ago by Langmuir.[14] The sources based on this principle have been used fairly extensively in studies of the reactions of atomic hydrogen with solid organic substances.[15,16] In order to improve the sensitivity, a number of workers have used a radioactive isotope (tritium) in their experiments.

The results of these studies are the basis of the method of synthesis of labelled preparations. The first experiments were performed with saccharides,[17] but the high yield of degradation products cast doubt on the practical value of the method. The main cause of the first failures was the use of thick targets which prevented the removal of heat from the reaction zone. The surface of the target was heated significantly both as a result of the absorption of the light emission from the filament and heat transfer through the molecular gas and as a result of the reactions of tritium atoms with the test substance. If effective removal of heat is ensured, the degree to which the test substance is preserved reaches 100% in some cases.[18]

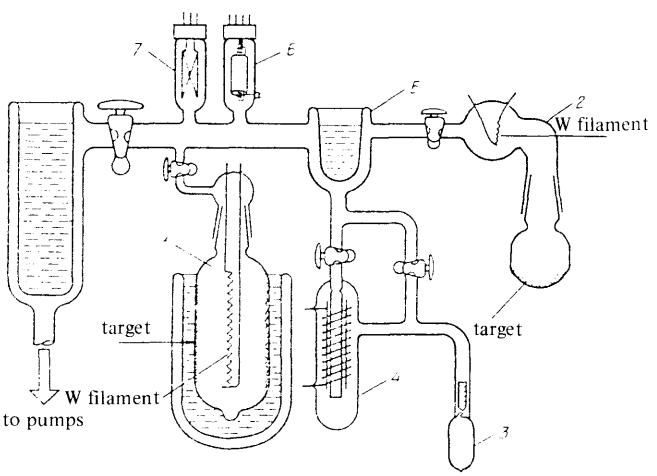


Figure 3. Apparatus for the preparation of labelled compounds with the aid of thermally activated tritium atoms: 1) vessel for the target used when the label is introduced under the conditions of direct light; 2) ditto for the introduction of the label into substances sensitive to light; 3) bulb with tritium opened by means of a metallic striker; 4) palladium leak valve for admitting measured amounts of tritium; 5) liquid nitrogen trap for freezing out condensable impurities; 6) and 7) pressure measuring sensors (thermocouple and ionisation sensors).

The apparatus used in such experiments is extremely simple (Fig.3) and consists of a glass cylinder with electrodes sealed into it between which is stretched a metallic (tungsten) filament heated electrically. A high vacuum is created in the cylinder, after which it is filled with tritium to the required pressure. The target substance is deposited on the inner walls of the cylinder cooled with liquid nitrogen or other cooling agents, which is necessary to prevent the access of the vapour of the test substance to the filament. The target film can be obtained by evaporating solutions or, what is more convenient for biopolymers, by lyophilisation. It is also possible to obtain frozen films of solutions, but it is then necessary to take into account the possible decomposition of the specimen as a consequence of the crystallisation of water during freezing. The undesirable effects can be avoided by employing rapid cooling of the target (for this purpose, it is best to use cooling agents other than liquid nitrogen) or by atomising the solution onto precooled walls. Satisfactory results are obtained when porous supports (filter or chromatographic paper, etc.) are used. The formation of a homogeneous film is then greatly simplified and the chemical and radiochemical yields are improved.[19]

In most cases reaction vessels with a comparatively small volume are used, since the establishment of the required pressure (10^{-2}–10^{-3} mmHg) then requires only a small amount of tritium. In such vessels the distance between the filament and the target is 3–4 cm. In larger vessels experiments with solid targets can be performed at room temperature. To prevent the incidence of direct light onto the specimen, the filament and the target are placed at an angle relative to one another.

Tritium is admitted into the reactor through capillaries, fine control high-vacuum valves, etc. It is best to use the so-called palladium leak valves in which molecular hydrogen diffuses through a palladium foil at an elevated temperature. This type of valve is extremely convenient for metering specified amounts and, furthermore, permits additional purification of the tritium. In the presence of a buffer reservoir it is possible to do without a leak valve altogether.

The conditions used in the introduction of the label differ little for different substances. The optimum results obtained when the temperature of the tungsten filament is 2000 K and heating is switched on for short periods (~15 s) with intervening cooling intervals (20–30 s). The tritium pressure is chosen to ensure that the atoms move from the filament to the target without colliding with molecules. This is associated with the dependence of the rate of the substitution reaction on the energy of the interacting particles. At a filament temperature of 2000 K, about 25% of the atoms formed have sufficient energy to react. The free path conditions for a distance between the filament and the target of ~3 cm are fulfilled at a pressure of ~5×10^{-3} mmHg. In the collisions between tritium atoms and target molecules unaccompanied by reaction the tritium atoms are also "cooled", as a result of which the label is localised in a thin surface layer whose thickness is ~5 Å,[20] and the attainment of high values of a requires the use of thin films of substance or the process must be frequently repeated, preparing anew a film of the substance already treated.

An increase of the temperature of the tungsten filament increases the fraction of the reactive species in the atomic beam. It can be shown that

$$n_{\varepsilon>\varepsilon_0} = \frac{2n\sqrt{\varepsilon_0}}{\sqrt{\pi(kT)^3}} \int_{\varepsilon_0}^{\infty} e^{-\varepsilon/kT} d\varepsilon = \frac{2n\sqrt{\varepsilon_0}}{\sqrt{\pi kT}} e^{-\varepsilon_0/kT}$$

where $n_{\varepsilon>\varepsilon_0}$ is the number of atoms in the beam with an energy greater than the specified limited ε_0 (activation energy) and n is the total number of atoms in the beam.

On the other hand, the rate of formation of tritium atoms itself increases ($T_2 \rightarrow 2T$); the activation energy for this process has been determined (see, for example, Brennan and Fletcher[21]) as 51.8 ± 1.0 kcal mol^{-1}, i.e. half the bond dissociation energy in the hydrogen molecule. For practical

purposes, one can employ the expression for the rate of atomisation

$$v_{at} = A\,(p)^{1/2} \exp(-\varepsilon/RT)$$

where $A = (1.5 \pm 0.5) \times 10^{2.5}$ atom cm^2 s^{-1} (mmHg)$^{-1/2}$ for tungsten, $\varepsilon = 51.8$ kcal mol^{-1}, and p is the hydrogen (tritium) pressure (mmHg).

For more rigorous calculations, the roughness coefficient, which according to most estimates is 1.4 for tungsten,[22] must be applied to the area of the filament calculated from its geometrical dimensions. Under the conditions described above at $T_{fil} \cong 2000$ K and a pressure of 5×10^{-3} mmHg, the quantity $v_{at} = 2.9 \times 10^{19}$ atom cm^{-2} s^{-1} and the beam of atoms onto the target is determined by the corresponding solid angle.

In apparatus of the type described it is usually possible to obtain, as a result of a single admission of tritium, preparations with an overall activity of 5–10 mCi; i.e. with $a = 10^3$–10^4 mCi g^{-1} for milligram amounts of the test substance. For biopolymers, for example, for proteins, this is an extremely high value (~10 Ci mmol^{-1}), which satisfies the majority of requirements. A great advantage of the method is the small consumption of tritium, which makes it possible to carry out experiments in radioisotope laboratories of any class.

IV. REACTIONS OF ATOMIC HYDROGEN

The main chemical reaction occurring when hydrogen atoms interact with saturated hydrocarbons is the abstraction of a hydrogen atom with formation of a free radical:

$$H + RH \rightarrow \dot{R} + H_2 \quad . \qquad (1)$$

The activation energy for this process is 6–8 kcal mol^{-1}.[23] For unsaturated compounds, hydrogen atoms should add to the multiple bond with a high efficiency, which also leads to the formation of a radical:

$$H + R{-}CH{=}CH{-}R' \rightarrow R{-}\dot{C}H{-}CH_2{-}R'. \qquad (2)$$

The activation energy for this reaction is 1–2 kcal mol^{-1}. Since the reaction results in the evolution of an amount of energy of ~40 kcal mol^{-1}, the radical formed is excited and can undergo various transformations, for example, can isomerise or decompose with dissociation of C–C or C–H bonds. In the case of functional derivatives of hydrocarbons, the spectrum of possible reactions is significantly broadened.

Not only primary processes but also subsequent reactions, leading to the formation of a labelled product, are evidently important for the synthesis of labelled compounds. The fate of the radicals formed via reactions (1) and (2) depends to a large extent on the experimental conditions: the phase state of the test substance, the temperature, and the chemical nature of the molecules of the medium. Thus the radical can enter into addition reactions with unsaturated compounds:

$$\dot{R} + R'{-}CH{=}CH_2 \rightarrow R'{-}CHR{-}\dot{C}H_2 \; . \qquad (3)$$

In chain reactions of this type, high-molecular-weight products are formed. When this is allowed by energy relations, the radical can abstract hydrogen or other atoms and groups of atoms from the molecules of the medium.

All the above reactions take place in both gas and liquid phases, but in the latter case account must be taken of the so-called cage effect, which limits the interaction of the radicals with one another and increases the probability of the stabilisation of the excited radicals but has little effect on the rates of reactions involving light hydrogen atoms.

In the reactions in the solid phase the differences become fundamental: the radicals formed are incorporated in the matrix and their subsequent fate depends on the properties of the latter. In a "soft" matrix, the diffusion of the radicals frequently limits the kinetic parameters of the entire reaction. In a "hard" matrix the translational movements and in many instances also the rotational movements of the radicals are hindered. This determines not only the quantitative characteristics of the rates of the processes but also the spectrum of the possible solid-phase reactions. Thus in a "hard" matrix there is relatively high probability of the stabilisation of the excited species as a result of the scattering of the energy, the intramolecular rearrangements of the type of *cis–trans*-isomerisation are hindered, etc. The lifetime of the radicals and hence their stationary concentration in a "hard" matrix are as a rule higher by several orders of magnitude than in the liquid and gas phases.

At the low temperatures usually employed for the synthesis of labelled preparations, the secondary reactions of the stable radicals with hydrogen atoms, whose mobility is fairly high even at ~100 K, assume an important role. As in the interaction of the radicals with one another, two processes are possible in this case:

$$RCH_2\dot{C}H_2 + H \rightarrow RCH_2CH_3 \text{ (recombination);} \qquad (4)$$

$$RCH_2\dot{C}H_2 + H \rightarrow RCH{=}CH_2 + H_2 \text{ (disproportionation).} \qquad (5)$$

However, the probabilities of these processes differ from those observed for the quadratic destruction of radicals—in many cases the rate of disproportionation is equal to or greater than the rate of recombination.[24]

In experiments involving the introduction of the label into organic substances, the target is usually thermostatted and the temperature (energy) of the tritium atoms is determined by the conditions of their generation. As a rule, the energy spectrum of the beam incident on the target corresponds to relatively high temperatures (ranging from room temperature to several thousands or tens of thousands of degrees) and this is responsible for their high reactivity. A decrease of temperature from 300 to 77 K should reduce the rate of reaction by a factor of ~10^{18}, i.e. almost to zero. However, it has been found that, even at temperatures close to 4 K, the rate of reaction is extremely high.[25] A detailed study showed that there are two mechanisms of the substitution of hydrogen by tritium, one of which obtains at relatively high temperatures (100–300 K) and is characterised by an activation energy of ~8 kcal mol^{-1}. At low temperatures (<100 K) the reaction with zero (0.3 kcal mol^{-1}) activation energy predominates, proceeding in all probability via a tunnel mechanism,[26] i.e. there is a possibility of completely different features of this reaction and other products may be formed. However, in the usual experiments the contribution of the tunnel reactions is small and can be disregarded.

In the region of high (≥1 eV) energies, direct substitution of hydrogen, first observed for recoil tritium atoms[27] and subsequently studied in detail,[6,28,29] proceeds together with reactions of types (1) and (2):

$$H^h + RH \rightarrow RH^h + H, \qquad (6)$$

where H^h is a hot atom. The process cross-section increases rapidly with increase of the energy and reaches a maximum at 10 eV. The use of reaction (6) for the preparation of labelled compounds is prevented by the lack of sources of hydrogen atoms with a suitable energy spectrum and intensity. Atoms capable of substituting hydrogen via mechanism (6) can be obtained by the photolysis of certain hydrogen-containing compounds (for example, HI and H_2S) or by exposure to radiation. It is also possible to use high-energy (~10^6 eV)

recoil atoms obtained as a result of nuclear transformations [for example, $^{6}Li(n\alpha)T$, $^{3}He(np)T$] and also special apparatus for the generation of beams of accelerated atoms and ions.

However, all these methods are in essence inapplicable to the introduction of a label into biologically active substances: exposure to radiation and recoil atoms is known to entail a considerable degradation of the initial compound, while apparatus with beams is extremely complex and the actual beam intensities are insufficient for the attainment of a high activity. Thus experimenters have at their disposal mainly sources of atoms with moderate energies, where the main primary process is reaction (1) and (or) (2).

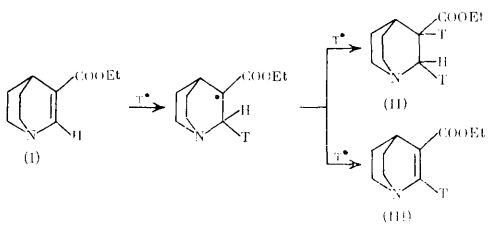
The reactions of hydrogen atoms with organic compounds have been described in detail in reviews.[30,31] Here we shall confine ourselves to the process, which plays an important role in the preparation of labelled compounds and which leads to the localisation of tritium in exchangeable groups of the type COOH, NH, NH_2, OH, SH, etc. Most of the tritium (90–99%) exists in this form and this fraction is independent of the chemical nature of the compound. Naturally such preparations cannot be used in practice without preliminary frequently fairly laborious purification. The mechanism of the reactions leading to the stabilisation of tritium atoms in the exchangeable groups is at present obscure. It may be that, as a result of stabilisation on the surface of a solid, the hydrogen atoms are polarised and interact in the form of a polar species predominantly with polar groups in the molecules of the medium. Such polarisation of hydrogen atoms has been demonstrated on the basis of EPR spectra.[31] The proposed mechanism is supported also by the finding that the coefficient of the introduction of the label into the polar groups depends little on the energy of the atoms.

V. PREPARATIVE SYNTHESIS OF LABELLED COMPOUNDS BY METHODS INVOLVING THE THERMAL AND HIGH-FREQUENCY ACTIVATION OF GASEOUS TRITIUM

As already stated, TAM and HFAM are universal methods for the introduction of the tritium label and are used to prepare labelled compounds belonging to a wide variety of classes. However, proteins (and also their fragments—peptides and aminoacids) have mainly attracted the attention of investigators and most of the studies in this field are devoted to such substances.

It was already stated above that, when organic compounds interact with tritium atoms generated under TAM and HFAM conditions, various reactions, regarded as side processes,[34–36] are observed together with the substitution of hydrogen by tritium (an analogous phenomenon has been noted also for other versions of the activation of gaseous tritium[3,32,33]). The relative contributions of the reaction involving the substitution of hydrogen by tritium and the side reactions depend greatly not only on the method of activation of T_2 (for example, the degree of addition to a double bond when the label is introduced by the Wilzbach method can be ten times greater than in the case where HFAM is employed[37]), but also on smaller changes in conditions within the framework of the same method. Thus the yield of addition products in TAM is influenced by the T_2 pressure, the temperature of the incandescent filament, the duration of exposure,[38,39] and even the character of the solvent used in the deposition of the specimen.[24] Structure factors are even more important: under identical conditions in the application of the HFAM, the ratio of the contributions of the reactions involving addition to the double bond and substitution of H by T is 2.6 for oleic acid, approximately 12 for unsaturated aminoacids, and only 0.02 for morphine.[37] This ratio can vary markedly even within the limits of a single series of compounds,[16,35] but, for simple alkenes and cycloalkenes, the saturation of the double bond as a rule proceeds more readily than the substitution of H by T.[16,35,36,39] Under TAM conditions, the substitution of H by T takes place with greater difficulty than the substitution of halogen atoms by T for both halogenoalkanes[40] and halogenobenzenes,[41] the ease of substitution of the halogen increasing in the sequence Cl << Br < I.

In a number of instances "side" reactions such as the saturation of double bonds and dehalogenation can be used for preparative purposes. Indeed, 3-ethoxycarbonyl-Δ^2-dehydroquinuclidine (I) has been converted by the TAM into the corresponding labelled saturated compound (II) and the unsaturated compound (III) in yields of 72 and 5.5% respectively:[42]



Other examples are the synthesis of labelled dihydrotestosterones from testosterone by the HFAM[43] and also the use of a high-frequency discharge (combined with heterogeneous catalysis) for the preparation of tritiated nucleoside monophosphates from the corresponding halides.[44]

The introduction of the tritium label into various classes of organic compounds is examined below.

1. Aliphatic Hydrocarbons

The study of the interaction of atomic tritium with aliphatic hydrocarbons was begun more than 20 years ago, but attention has been concentrated on the theoretical study of the reactions involved and not on the preparative synthesis of labelled compounds. In the early studies it was already shown that for alkanes (pentane and hexane) the degree of dissociation of the carbon–carbon bonds under the influence of tritium atoms, generated under both TAM[45] and HFAM[12] conditions, is much smaller than under the conditions of the Wilzbach method or in reactions with hot tritium atoms.[46] The main process is the substitution of hydrogen by tritium and in the TAM (temperature of W filaments 1750 °C)[45] hexane-*t* and pentane-*t* are obtained in yields greater than 80%. The mechanism of the substitution reaction evidently involves the abstraction of a hydrogen atom from the alkane ($RH + T^{\cdot} \rightarrow R^{\cdot} + HT$) and recombination ($R^{\cdot} + T^{\cdot} \rightarrow RT$). An alternative version is also possible—disproportionation of the alkyl radicals into an alkane and an alkene with subsequent addition of a T atom to the alkene, but the contribution of this mechanism at low temperatures is apparently small, which has also been confirmed by the low yields (5–10%) of high-molecular-weight products.[45] However, when the temperature of the specimen is increased to 90 K, the contribution of the disproportionation reaction increases sharply.[47] The first stage, namely the abstraction of a hydrogen atom, proceeds more readily at a tertiary carbon atom than at secondary and primary carbon atoms.[48]

In the case of cycloalkanes the addition of tritium, leading to the rupture of the carbon ring and the formation of a labelled alkyl radical, competes with the hydrogen abstraction reaction. The degree of this reaction is determined primarily

by the ring strain: under identical TAM conditions, the yield of cyclohexane-*t* from cyclohexane was ~80%,[45] while cyclopropane[49] was converted into cyclopropane-*t* only in 37% yield and the remaining labelled products consisted of acyclic hydrocarbons formed from the $TCH_2CH_2\dot{C}H_2$ radical. The reaction of cyclohexane with T_2 under HFAM conditions also leads to the formation of cyclohexane-*t* as the main labelled product.[12] The energy of the tritium atom plays a very significant role:[49] at a temperature of the tungsten filament of 1180 °C, only ethane-*t* and propane-*t* are formed from cyclopropane in proportions of 73 : 27, their contents among other products being reduced at 1520 °C to 37 and 50% respectively (the content of cyclopropane-*t* is ~14%) and cyclopropane-*t* becomes the main product (37%) only at 1750 °C, but the content of propane-*t* also rises to 23%.

In the interaction of cyclohexane with tritium atoms under TAM conditions at 1800–2250 K, the main labelled products, apart from cyclohexane-*t*, are also cyclohexene-*t* and bicyclohexyl-*t*.[50] Thus the cyclohexyl radicals obtained as a result of the abstraction of hydrogen from cyclohexane (activation energy $E_a \cong 7$ kcal mol^{-1}) enter into all possible reactions—recombination, disproportionation, and dimerisation.

As already noted, the addition of tritium atoms to the double bond in alkenes and cycloalkenes proceeds more readily than the substitution of H by T. For example, E_a for addition to cyclohexene is lower by a factor of 2–4 than for the substitution reaction[36] and the main product (~70%) of the reaction of cyclohexene with T_2 under TAM conditions is cyclohexane-*t*.[36,45,51] Analogously, hex-1-ene is converted in ~70% yield into hexane-*t*.[45] It has been suggested[15] that the saturation of the double bond takes place in two stages—tritium adds in succession initially to the alkene and then to the radical formed.

Considerable differences in the ease of saturation of double bonds have been noted for different alkenes:[15,16,35] propene reacts particularly rapidly, but-1-ene, isobutene, and methylbut-1-enes react more slowly, while the reactions of buta-1,3-diene, pent-1-ene, and finally hex-1-ene are slower still. These differences evidently reflect the differences between the values of E_a at low temperatures.[15] The substitution of hydrogen, whose contribution is ~25% for cyclohexane and hex-1-ene,[45] and the migration of the double bond,[24,34,35] compete with the alkene saturation reaction. It has been suggested[16,24,34,50] that tritium initially adds on to form a labelled alkyl radical, which is then converted into a labelled alkene as a result of the loss of H on interaction either with a T atom or (which is less likely) with another alkyl radical. This mechanism also explains the isomerisation of alkenes under the influence of tritium atoms observed for but-1-ene[34,35] and cyclohexylcyclohexane:[24]

$$RCH{=}CHCH_2R' \xrightarrow{T} RCHT{-}\dot{C}HCH_2R' \xrightarrow{T} RCHTCH{=}CHR' .$$

The direction of isomerisation is determined by thermodynamic factors: but-2-ene does not isomerise to but-1-ene under these conditions.

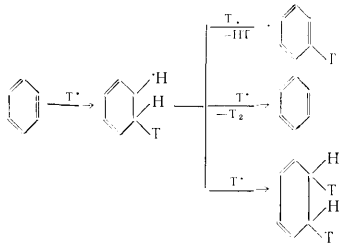
The data for alkynes are restricted to those for acetylene,[12] which is labelled by tritium under HFAM conditions without the saturation of the triple bond. When the TAM (tungsten filament, 2000 °C) is used, labelled saturation products—ethane and ethylene (25–30 and 18% respectively)—predominate and the yield of HC≡CT falls to 18%.

The reactions of atomic tritium with functional derivatives of aliphatic hydrocarbons have been very little studied. Apart from the halogenopentanes already mentioned as well as aliphatic acids, carbohydrates, and aminoacids (dealt with in separate sections—see below), there are only a few examples. Triethyloxonium tetrafluoroborate $Et_3O^+BF_4^-$ readily exchanges its hydrogen atoms for tritium under TAM conditions (2200 °C, T_2 pressure ~0.01 mmHg).[19,52] The labelled preparation had a high value of a (~5 Ci mmol^{-1}), contained no labile tritium, and did not require special purification, because all the theoretically possible cleavage or hydrolysis products are volatile substances and are removed under the experimental conditions.

Tritium-labelled sodium dodecyl sulphate ($n\text{-}C_{12}H_{25}OSO_3Na$) with $a = 0.014$ Ci g^{-1} has also been obtained by the TAM, a film of a frozen aqueous solution being bombarded.[53] A label has been introduced into dicyclohexylurea ($a = 0.178$ Ci mmol^{-1}) with the aid of the HFAM (pulse discharge, 800 kHz, T_2 corresponding to 25 c) but only ~20% of the tritium introduced was contained in the cyclohexane rings.[54]

2. Aromatic Compounds

The powerful activating influence of the discharge on the incorporation of tritium into aromatic compounds placed in T_2 was already noted comparatively long ago[55–57] and appreciable decomposition of the test substances was not observed. Aromatic compounds also do not decompose under TAM conditions (temperature of tungsten filament 1460 °C, pressure 0.001–0.005 mmHg)[58] but in many instances the saturation of the aromatic ring takes place vigorously. For example, labelled benzene, cyclohexene, and cyclohexane have been obtained from benzene (temperature of tungsten filament 1750 °C, pressure ~0.01 mmHg, their radioactivities being distributed in proportions of 21 : 35 : 39.[45] Evidently labelled cyclohexadienyl radicals (IV) are formed initially:



(7) (8) (9)

(IV)

Their subsequent interaction with tritium atoms can lead to the formation of labelled benzene, unlabelled benzene, or labelled cyclohexadiene, which is converted into labelled cyclohexenes and cyclohexane on combining with more tritium. The formation of cyclohexadienyl radicals on addition of excited H(T) atoms to aromatic compounds has been confirmed by EPR.[48,59,60] The relative contribution of reaction (7) is small and the radiochemical yield of benzene-*t* under these conditions does not exceed 5%.[58] In the reactions involving alkylbenzenes the substitution of H in the side chain competes with the saturation of the aromatic ring. Although this reaction, in the first stage of which H is abstracted with formation of the corresponding benzyl radicals, proceeds much more slowly than the addition to the ring,[61] it is the main process leading to the formation of labelled alkylbenzenes. With increase of the number of alkyl groups, the ability of this reaction to compete increases (i.e. in the sequence benzene < toluene < *o*-xylene < mesitylene).[58]

Thus in labelled alkylbenzenes tritium is localised mainly in the side chain (55–67% T for toluene-*t* when the HFAM is used).[62] An analogous phenomenon has been observed[63,64] for labelled aromatic aminoacids (see below). It is of interest that, in other versions of isotope exchange involving alkylbenzenes (the Wilzbach method, reaction with hot atoms,

exchange initiated by ultraviolet light or γ-radiation, and acid catalysis in solution), tritium is localised mainly in the aromatic ring.[62,65]

In addition substituents hinder (under the influence of both electronic and steric factors) the addition of tritium to the ring.[48,58] The H(T) atom never enters the position in the ring where a substituent is present and attacks only the *ortho*- or *para*-positions.[48] On the other hand, the addition to the *meta*-position is difficult, which evidently explains the greater tendency towards the addition of H(T) to 1,3-disubstituted benzenes compared with the 1,2- and 1,4-disubstituted derivatives.[48] Probably, for the same reason the aromatic ring is not involved when the tritium label is introduced into the alkaloid morphine by the HFAM.[37]

Thus when the HFAM and TAM are used, the introduction of the tritium label into aromatic compounds proceeds with greater difficulty than in the case of aliphatic hydrocarbons and it is as a rule impossible to attain high values of a. This is confirmed by the data in Table 1, which includes, together with aromatic hydrocarbons, also aromatic heterocycles—acridine and xanthine. It is significant that, under the conditions presented in Table 1, values of a greater by a factor of 50–100000 (for the HFAM) and 10–50 (for the TAM) had been obtained for certain labelled compounds of other classes under the conditions presented in Table 1.[10,19] Although the TAM is more suitable for the preparative synthesis of labelled aromatic compounds, rigorous comparative studies have not been carried out.

Table 1. Labelled aromatic compounds.

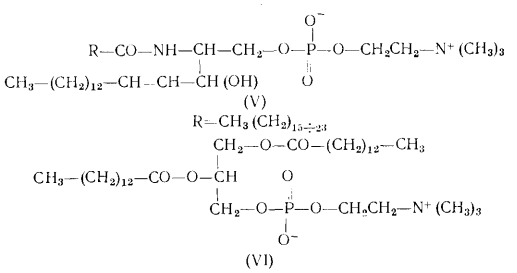
Compound	a, m Ci mmol^{-1}	Refs.
Acridine	0.045	[10]
p-Aminobenzoic acid (Na salt)*	35	[66]
Ethyl *p*-aminobenzoate*	135	[19, 66]
p-Aminosalicylic acid	0.045	[57]
Anthracene	0.515	[10]
Benzoic acid	3.8	[10]
Xanthene	0.423	[10]
9-Methylanthracene	0.04	[10]
Naphthalene	0.01	[10]

*The substance was deposited on a paper support; method of preparation—TAM; in the remaining cases the HFAM was used.

In conclusion we shall point out the likely usefulness of the synthesis of tritium-containing aromatic compounds from halogeno-derivatives. The tritium atoms generated under the TAM conditions substitute the halogen atom in halogenobenzenes; the yields of the substitution products for iodobenzene and bromobenzene are respectively 2.8 and 1.5 times greater than for chlorobenzene,[41] which agrees with the C–Hal bond dissociation energies in the above series.

3. Lipids and Aliphatic Acids

The question of the introduction of the tritium label into lipids is a matter of considerable urgency but the attempts at the direct introduction of tritium by the TAM and HFAM have so far not met with notable success. This can apparently be explained by the extensive cleavage of lipids under the conditions of their interaction with excited tritium atoms (for example, the complete decomposition of egg lecithin and dimyristoylphosphocholine has been observed[67]) and also by the presence in certain lipid molecules of residues of unsaturated aliphatic acids. Nevertheless, labelled sphingomyelin (V) (a = 0.2 c mmol^{-1}) and 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (VI) (a = 0.02 c mmol^{-1}) have been obtained[67] by the TAM. In the case of sphingomyelin the presence of an admixture of labelled dihydrosphingomyelin, which does not preclude further use of the preparation, was not specially tested for. On the other hand, despite the low value of a, the experiment with lecithin (VI) may lead to new prospects for preparative synthesis: although compound (VI) decomposed fully under the influence of tritium atoms after being deposited on the surface of a glass vessel,[67] after the deposition on a paper support the yield of the labelled preparation proved to be almost quantitative:[19]



(V)

(VI)

Another method of synthesis of labelled lipids consists in the employment of labelled aliphatic acids, which makes it possible, in particular, to obtain phospho-lipids containing simultaneously the radioactive label and photoreactive groups,[67,68] The results of the use of the TAM and the HFAM for the introduction of tritium into aliphatic acids are presented in Table 2.

Table 2. Labelled aliphatic acids.

Compound	Method	a, m Ci mmol^{-1}	Refs.
11-Aminoundecanoic acid	TAM	300	[67, 68]
Isocaproic acid (Na salt)	HFAM	19.4	[10]
Methyl 12-hydroxystearate	TAM	15	[67]
Oleic acid	HFAM	0.832	[10]
Stearic acid	ED	0.026	[69]

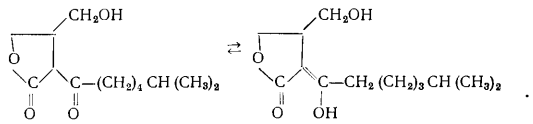
Note. In the TAM the temperature of the tungsten filament was 2000 °C and the walls of the vessel were cooled with liquid nitrogen; the parameters of the HFAM were 2450 MHz and 20 W; ED—excitation with an electric discharge (pressure 100 mmHg).

Appreciable decomposition of carboxylic acids under the conditions of their interaction with tritium atoms has been noted[67,70] and is apparently associated with the abstraction of hydrogen from the carboxy-group: the acyloxy-radicals RCOO$^{\cdot}$ formed are known to be readily cleaved into CO_2 and R$^{\cdot}$. The replacement of the free acids by their salts or esters sharply reduces the degree of decomposition: the yield of the labelled methyl ester of 12-hydroxystearic acid is 75% under conditions where the acid itself is fully

decomposed.[67] As can be seen from Table 2 for 11-aminoundecanoic acid, which is an inner salt, the binding of the carboxy-group also makes it possible to achieve higher values of a.

The mechanism of the incorporation of tritium into the hydrocarbon chain of saturated aliphatic acids is the same as for alkanes. The formation of radicals as a result of the abstraction of H from the carbon atoms in malonic and methylmalonic acid under the HFAM conditions has been confirmed by EPR.[71] As for alkenes, for unsaturated aliphatic acids the addition reaction predominates over the substitution reaction. When the HFAM is applied to oleic acid, labelled stearic and oleic acids are formed in proportions of 2.6 : 1, but the ratio is much greater when the Wilzbach method is used (24.4 : 1).[37]

The so-called A-factor (VII)—the substance which regulates the biosynthesis of the antibiotic streptomycin—should also be included among aliphatic acid derivatives. The labelled A-factor has been obtained[19] in ~30% yield with $a = 0.26$ c mmol^{-1} (TAM, paper support) and saturation products which might have been formed from the enolic forms of the A-factor were not detected:



(VII)

4. Low-Molecular-Weight Bioregulators

The tritium label has been introduced into low-molecular-weight bioregulators (steroids, alkaloids, antibiotics, etc.) only with the aid of the HFAM. The labelled A-factor, the synthesis of which was described above, can be regarded as the only exception#.

For steroids (corticosterone and progesterone), the classical version of the HFAM (2450 MHz, 0.7 mmHg, T_2 corresponding to 80 mCi, 5 min) yielded low results: although the chemical yield was 60–65%, the radiochemical yield did not exceed 1% and $a = 0.0025$–0.003 Ci mmol^{-1}.[75] When the HFAM was used in the case of aflatoxin,[76] similar values of a were achieved, but these increased markedly with increase of the surface area (with the use of a glass paper support), with decrease of the size of the test sample, and with increase of the T_2 pressure. Thus labelled 6-azido-6-dehydrodexamethasone and 21-diazo-21-deoxycorticosterone (0.15 mg, deposition on glass paper, pressure 9 atm) have been obtained by means of the HFAM with $a \cong 1$ Ci mmol^{-1}.[43] It is extremely important that the highly reactive $-N_2$ and $-N_3$ groups are not involved under HFAM conditions. On the other hand, under the same conditions in the case of testosterone the isotope exchange is accompanied by the addition of T_2 to the $\Delta^{4,5}$-bond with formation of labelled 5α- and 5β-dihydrotestosterones.[43]

On the other hand, the double bond in the alkaloid morphine is hardly saturated under HFAM conditions and morphine-t is formed with $a = 0.0027$ Ci mmol^{-1} (for a sample of 1 mg).[37,77] Better results were achieved for the alkaloid 1-cocaine ($a \cong 0.03$ Ci mmol^{-1}), while the local anaesthetics which are its analogues (carbocaine, xylocaine, citanest, tetracaine, and procaine) are labelled less successfully.[78,79]

5. Carbohydrates

The few attempts at the preparative synthesis of labelled carbohydrates by exposure to atomic tritium cannot be recognised as entirely successful, since the values of a for the labelled compounds obtained proved to be low; however, the results achieved are no worse than those obtained when the Wilzbach method is used. Glucose, sucrose, glucose-1-phosphate ($a = 0.006$–0.008 Ci g^{-1}) as well as starch grains[80] (both amylose and aminopectins proved to be labelled) have been labelled with the aid of the TAM;[17] the HFAM has been used to introduce tritium into methyl-β-D-glucoside [a 99 : 1 mixture of He and T_2 and a electrodeless ring discharge (40 mHz) were used], with a radiochemical yield of ~2% and $a = 0.006$ c mmol^{-1},[9] and into dextran (tritium corresponding to 0.5–2 Ci, 1–4 mmHg, 2450 MHz, $a = 0.2$ Ci mmol^{-1}).[76] Under identical conditions, peptides and proteins are labelled to a much greater extent than carbohydrates.[9,76]

Table 3. Labelled nucleic bases, nucleotides, and nucleic acids.

Compound	m, mg	Consumption of tritium, c	Conditions	a, Ci mmol^{-1}	Refs.
Adenine	110	0.08	2450 MHz, 150 W, 0.7 mmHg, 5 min	0.021	[75]
Thymine	80	0.08	ditto	0.0048	[75]
ATP	100	25	800 kHz (pulse conditions), 200 mmHg	0.03	[81]
Guanosine monophosphate	—	—	2000 K, 0.01 mmHg, 2–5 min	10–20	[18]
Deoxycytidine tri-phosphate	—	—	99 : 1 He–T_2 mixture, 80 W, 40 MHz, 0.01 mmHg, 1 h	0.5	[82]
p-Nitrophenyl ester of AMP	—	—	ditto	0.001	[82]
ATP-3′-OCH$_3$	—	—	"	1	[82]
λ phage DNA	—	—	"	0.08	[82]
Total tRNA	—	—	"	0.01	[82]
tRNA from *E. coli*	1	30	2200 K, 0.01 mmHg, 0.5 min	0.3	[19]

Remarks. Labelled guanosine monophosphate and tRNA from *E. coli* were prepared by the TAM, while in the remaining cases the HFAM was used; the chemical yields of adenine and thymine were 85 and 80% respectively, while in the remaining cases the yield was 50% (not indicated for guanosine monophosphate); the radiochemical yields were 21% for adenine, 0.02% for tRNA for *E. coli*, and 3.6% for thymine; in the remaining cases the radiochemical yield was not indicated.

6. Nucleic Bases, Nucleotides, and Nucleic Acids

The direct introduction of tritium into nucleic acids and nucleotides is extremely important in view of the role which these compounds play in biological processes and the large number of studies in which they are employed. It has been shown[75] that the HFAM is much more convenient for this purpose than the Wilzbach method and subsequently the introduction of tritium into certain nucleic bases, nucleoside monophosphates, and nucleic acids with the aid of both the

#There are also reports[72–74] of the use of the TAM for the preparation of the tritium-labelled alkaloid aconitine and tetrodotoxin (the venom from the Fugu fish) with $a \cong 0.5$ c mmol^{-1}, but no experimental data are presented in these communications.

HFAM and the TAM was investigated; the results are presented in Table 3. The extent to which compounds of this class remain undamaged under HFAM and TAM conditions is high but polymeric molecules can be modified without cleavage. In particular, there is a possibility of the addition of tritium to the unsaturated bonds of the heterocyclic DNA and RNA nuclei because solid thymine and uracil form free radicals by combining with hydrogen atoms in a discharge in gaseous hydrogen.[83]

It is also noteworthy that a high-frequency discharge has been used[44,81] for the activation of T_2 in the synthesis of labelled nucleoside monophosphate and uracil by solid-phase reductive dehalogenation. Under HFAM conditions, the pyrophosphate bonds in adenosine triphosphate are ruptured with formation of adenosine diphosphate and adenosine monophosphate (in yields of 22 and 7% respectively), the values of a of which exceed that of labelled adenosine triphosphate by factors of ~1.5 and ~2 respectively.[81]

7. Aminoacids, Peptides, and Proteins

It was already stated above that the reactions with atomic tritium are of special interest as a method for the introduction of the label into proteins. A high degree of radioactivity can be introduced into the protein molecule also with the aid of ^{125}I or ^{131}I, but, firstly, the iodinated proteins are chemically (and frequently biologically) no longer identical with the native proteins, and secondly, the protein iodination methods used until recently involve oxidative reactions.

The synthesis of tritium-containing proteins is also difficult. The biosynthesis of the required product in any kind of satisfactory yield is possible only in a few instances and requires the employment of very high radioactivities of the HTO water and isolation and purification by extremely laborious and carefully elaborated methods. The scope of the chemical synthesis of proteins labelled with tritium is also limited. The greatest successes have been achieved[3] in the case of peptide hormones and toxins, containing up to several tens of aminoacid residues, into the molecules of which tritium had been introduced by the combination of peptide synthesis (from halogenoaminoacids) and catalytic dehalogenation. On the other hand, the exchange methods, particularly the thermal and high frequency activation of gaseous tritium, whose advantages have already been considered in the Introduction, are the most promising and universal for the synthesis of tritium-containing proteins.

Since the interaction of atomic tritium and proteins can involve various processes which depend on the primary, secondary, and tertiary structure of the protein molecules, the study of the general characteristics of this reaction was begun with model compounds—aminoacids and short peptides.[18,78,84] Table 4 shows that, with the aid of the TAM and the HFAM, it is possible to label both aliphatic and aromatic aminoacids. According to the results for alanine and phenylalanine, the TAM makes it possible to achieve higher values of a, but the comparative advantages of the TAM and HFAM for the preparative synthesis of labelled aminoacids have not been specially studied.

Apart from the reaction involving the direct substitution of H by T (Table 4), the reduction with atomic tritium of unsaturated C=C bonds and certain functional groups has also been used for preparative purposes. Thus, under HFAM conditions (20 W, 2450 MHz, T_2 equivalent to 1 Ci, 5 min), 3,4-dehydro-DL-proline undergoes mainly an addition reaction with formation of labelled DL-proline,[37] while DL-alanine-t (a = 0.0004 Ci mmol^{-1}) was the only labelled product of the interaction of α-hydroxyiminopropionic acid with HT (8000 W, 40 mmHg, 10 min).[89] The synthesis (HFAM, 1.5 keV, working gas—hydrogen with an admixture of 0.0001% of tritium, pressure 5×10^{-4} mmHg, 30 min) of labelled phenylthiohydantoin derivatives of aminoacids $RCH(NH_2).CON(Ph)C{=}S$ [13] in 1–10% yield and with $a \cong 0.001$ Ci g^{-1} should also be mentioned. The intramolecular distribution of tritium between the aminoacid residue and the phenyl group was not determined.

Table 4. Labelled aminoacids.

Aminoacid	Method	τ, min	φ, %	η, %	a, Ci mmol^{-1}	Refs.
Alanine	A	6	83	2.2	0.0016	[75, 78]
Alanine	B	—	55	—	0.05	[81]
Alanine	C	—	—	4	0.2	[9]
Alanine	D	60.17	—	—	0.65	[70, 85, 86]
Arginine	B	—	42	—	0.055	[81]
Aspartic acid	B	—	—	—	0.1	[81]
Valine	B	—	—	—	0.043	[81]
Valine	E	15	—	—	0.087	[87]
Histidine	B	—	15	—	2.32	[81]
Glycine	A	6	60	1	0.0006	[75, 78]
Glutamic acid	B	—	—	—	0.14	[81]
Isoleucine	B	y—	47	—	0.075	[81]
Leucine	A	12	72	10.2	0.0107	[75, 78]
Leucine	B	—	—	—	0.085	[81]
Leucine	E	—	—	—	0.13	[76]
Methionine	B	—	—	—	0.23	[81]
Proline	B	—	20	—	0.38	[81]
Proline	E	15	—	—	0.25	[87]
Serine	B	—	—	—	0.035	[81]
Tyrosine	B	—	—	—	0.35	[81]
Tyrosine	D	—	—	—	0.315	[88]
Tryptophan	A	0.5	64	8.9	0.0145	[75, 78]
Tryptophan	B	—	45	—	0.062	[81]
Phenylalanine	A	6	76	9	0.0119	[75, 78]
Phenylalanine	B	—	—	—	0.165	[81]
Phenylalanine	D	—	—	—	0.3	[88]
Cystine	B	—	30*	—	0.03	[81]

Remarks. Methods: A—microwave discharge (150 W, 2450 MHz), T_2 equivalent to 0.08 Ci, pressure 0.7 mmHg, DL-aminoacid sample 100 mg; B—microwave discharge under pulse conditions, T_2 equivalent to 25 Ci, pressure 200 mmHg, DL-aminoacid sample 100–150 mg; C—electrodeless ring discharge (80 W, 40 MHz), 99:1 He–T_2 mixture (pressure in the region of target 10^{-4} mmHg), sample 5 mg; D—TAM, temperature of tungsten spiral 2000 K, pressure 10^{-2} mmHg, sample 0.2–1.0 mg; E—microwave discharge (30 W, 2450 MHz), circulation conditions (190 circulations per minute), T_2 equivalent to 0.5–2.0 Ci, pressure 1–4 mmHg. In the case of proline and valine (the L-aminoacid samples were 0.1–0.4 mg each) the test substance was deposited on a paper membrane.

Notation: τ is the duration of exposure and ϕ and η are respectively the chemical and radiochemical yields.

*Cysteine (a = 0.316 Ci mmol^{-1}, yield 50%) was obtained together with cystine.

As regards the influence of the experimental conditions, it has been established for the TAM (Table 4, procedure D)[86] that a increases by a factor of approximately 7 with increase of the temperature of the film of the deposited substance from 77 to 300 K (in relation to tyrosine). For the HFAM (procedure A), a change in sample size (from 13 to 100 mg) is only slightly reflected in the value of a but leads to an approximately fourfold increase of the radiochemical yield,[78] while in the case of labelled L-proline (TAM, procedure D) an increase of the sample size from 0.1 to 1 and 10 mg entails a decrease of a by factors of ~2 and ~10 respectively.[87] In

procedure A, the variation of the power of the discharge (within the limits 50–200 W) and of its duration (in the range 3–12 min) has little influence on a and on the radiochemical yield, but both these parameters decrease by a factor of almost 2 with decrease of the time of exposure to 1 min.[78] A twofold increase of the pressure makes it possible to increase a by a factor of 2 but a subsequent increase of the pressure is less effective and for 0.96 c/T_2 the value of a is only slightly greater than for 0.08 c, while the radiochemical yield falls by a factor of ~10. The amount of labile tritium in the labelled aminoacids depends greatly on the reaction conditions. Thus alanine-t, obtained by methods C [9] and D,[86] contained respectively 60 and 90–95% of labile tritium.

The mechanism of the reaction of aminoacids with atomic tritium has been studied almost exclusively under TAM conditions. According to general ideas (see above), in the first stage attack on the molecule of the aminoacid $RCH_2CH(NH_2).COOH$ by the tritium atom results in the abstraction of hydrogen and the formation of HT and the radical $RCH_2\dot{C}.(NH_2)COOH$ (VIII) or $RCHCH(NH_2)COOH$ (IX), which are converted into labelled aminoacids in the second stage on recombination with the tritium atom. The first stage is rate-limiting and the relative contributions of the reactions involving the formation of radicals (VIII) and (IX) can be inferred from the intramolecular distribution of tritium between the α- and β-positions in the labelled aminoacids. Data for such intramolecular distribution in the case of the TAM are presented in Table 5. In all cases the formation of radicals of type (IX) is energetically more favourable, which agrees well with calculated data,[63,64,90] which indicate a greater stability of compound (IX) (greater degree of delocalisation of the unpaired electron) and also a greater mobility of the hydrogen atoms in the β-position (in all cases except alanine; the limiting electron density was used as the criterion). These results also agree with the known behaviour in the formation of free radicals: the abstraction of H from the CH_3 group is more difficult than from the substituted CH_2 group (cf. data for alanine). The influence of substituents in the introduction of tritium into aminoacids by the TAM (see Table 4) is on the whole the same as in the reaction of aminoacids with hydrogen atoms in aqueous solution.[91]

Table 5. Intramolecular distribution of tritium (%) in the labelled aminoacids $R\overset{\beta}{C}H_2\overset{\alpha}{C}H(NH_2)COOH$ obtained with the aid of the TAM.

Aminoacid	R	α-Position	β-Position		Aromatic ring	Refs.
			per C–H bond	total		
Alanine	H	43	19	57	—	[63, 73]
Serine	OH	18	41	82	—	[63, 73]
Cysteine	SH	11	45	89	—	[63, 73]
Aspartic Acid	COOH	30	35	70	—	[63, 73]
Phenylalanine	Ph	5	19	38	57	[90]
Tyrosine	p-HOC_6H_4	8	42	84	8	[64, 88]

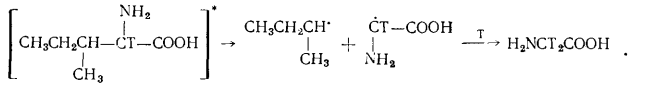
The preferential localisation of tritium in the β-position has been observed[92,93] also for labelled L-isoleucine, L-alloisoleucine, and L-valine obtained with the aid of the HFAM. In the case of valine tritium was distributed among the α-, β-, and γ-positions in proportions of 7 : 33 : 60 (i.e. 10% for each γ-C–H bond).

As regards the intramolecular distribution of tritium in labelled aromatic aminoacids—phenylalanine and tryosine (Table 5), the much greater radioactivity of the aromatic ring in phenylalanine can be readily accounted for, because, as already mentioned above, the ring substituent (in the given instance OH in tryosine) greatly hinders the addition of tritium (the rate-limiting stage).

More detailed ideas about the mechanism of the interaction of atomic tritium with aminoacids are based on the fact that the kinetics of the reactions of tritium atoms (formed by the TAM) with phenylalanine and tyrosine at a temperature <200 K deviate from the Arrhenius equation,[88,94] while at a temperature ≤60 K, the rate of reaction is altogether independent of temperature, although even at 30 K these reactions proceed at an appreciable rate.[72,95] The low-temperature kinetic limit indicates a tunnel mechanism (see above). It has been suggested[72,95] that the tunnel effect predominates at temperatures ≤200 K. This is confirmed by the dependence of the intramolecular distribution of tritium in labelled aromatic aminoacids on temperature.[88,95] For tyrosine at 300–400 K and for phenylalanine in the range 77–300 K, a change in the distribution of tritium between the aromatic ring and the side chain is also observed when the duration of exposure is altered,[88,94] which is associated with the losses of tritium from the ring as a result of disproportionation.

The side processes in the interaction of atomic tritium with aminoacids involve the cleavage of the C–C bonds with formation of labelled molecules having a lower molecular weight, the substitution of functional groups by tritium (decarboxylation, deamination, deoxygenation, and desulphurisation), stereoisomerisation, and also the addition of tritium to the aromatic ring and the dissociation of sulphide bridges. The extent of these processes depends both on the reaction conditions and on the structure of the aminoacids.

The cleavage of the carbon skeleton has been observed in many instances. Thus, under the TAM conditions, labelled propane and ethane[86] are formed from alanine, while labelled benzene, toluene, as well as glycine and alanine[94,96] are formed from phenylalanine, the last two acids being obtained also from tyrosine under the same conditions.[94] In many instances the cleavage is apparently caused not by tritium but by the emission from the incandescent tungsten spiral.[94] However, the shortening of the aminoacid chain leading to the formation of lower homologues is a true side reaction and its character is general. Under HFAM conditions, the formation of labelled glycine from L-valine[93] and L-alloisoleucine[92] has been observed; labelled glycine, containing ~20% of the total radioactivity has been obtained from L-isoleucine; it was formed as a result of the cleavage of the excited L-[2-T]isoleucine molecule:[92]



The substitution of functional groups by tritium atoms is also a general process for all aminoacids. As a result of the substitution of the carboxy-groups under TAM conditions, labelled phenylethylamine and tyramine, containing up to 10% of the total radioactivity, are obtained from phenylalanine and tyrosine respectively.[94,96] Deamination under the same conditions leads to the formation of labelled aliphatic acids: propionic acid from alanine,[85] phenylpropionic acid from phenylalanine and tyrosine (in the latter case the phenolic hydroxyl is also replaced by tritium),[94,96,97] and γ-aminobutyric acid from α,γ-diaminobutyric acid,[73] for which deamination is difficult in an acid medium. This agrees with the mechanism[95,97] according to which the tritium atom initially adds to the amino-group and then NH_2T is split off. The

substitution of the hydroxy-group in tryosine by tritium (TAM) leads to the formation of labelled phenylalanine[94] and in the case of cystine (HFAM), the sulphide bridge is readily cleaved with formation of labelled cysteine whose yield and radioactivity (Table 4) exceed the corresponding values for the labelled cystine obtained simultaneously.[81]

The addition of thermal hydrogen atoms to the aromatic rings of L-phenylalanine, L-tyrosine, and DL-tryptophan at 77 K has been detected by EPR.[60] When phenylalanine is tritiated by the Wilzbach method, labelled β-cyclohexylalanine is the main side product,[98] but under TAM conditions the benzene ring of phenylalanine or tyrosine is not saturated.[94]

The question of the racemisation of optically active aminoacids in the course of the introduction of tritium is particularly important, because it determines the suitability of the method for the preparation of tritium-containing proteins with retention of their biological activity. In general, in the reactions of tritium with solid L- or D-aminoacids, the degree of formation of the labelled optical isomer is low. In the Wilzbach method it varies from 1 to ~20%[98,99] and in the HFAM it is even smaller (for example, it amounts to 1.5% for L-valine compared with 4.0% in the Wilzbach method),[93] while the inversion of the configuration at the α-C-atom in L-isoleucine and L-alloisoleucine takes place to the extent of 1.0 and 0.3% respectively.[92] This can be explained by the fact that the α-positions in aminoacid molecules are attacked by tritium atoms only to an insignificant extent—1% for L-alloisoleucine and <8% for L-isoleucine. The predominant attack on the β-position is, however, associated also with the greater degree of epimerisation at the asymmetric β-C-atom. Thus, under HFAM conditions, labelled L- and D-isoleucines and L- and D-alloisoleucines are formed from L-isoleucine in proportions of 72 : 1 : 23 : 4 (in terms of radioactivity), while the same stereoisomers are formed from L-iso-leucine in proportions of 29 : 0.3 : 67 6 : 3.[92]

The racemisation of optically active aminoacids under TAM conditions has been investigated only in relation to L-alanine,[100] which formed a mixture of labelled L- and D-alanines (~70 : 30) at a target temperature of 77 K, while after the introduction of the label by the HFAM (under the conditions of charge transfer involving atomic ions accelerated to an energy of 0.6 keV) the aminoacid did not racemise although it contained ~25% of the added tritium in the α-position. From this, the authors[100] assume that tritium atoms with an energy >1.5 eV interact with aminoacids as a result of direct synchronous substitution of H by T and not via a radical mechanism.

It is noteworthy that the products of the side reactions are dominant overall. For example, the yield (as a percentage of the total radioactivity) of labelled phenylalanine (labelled by the TAM) is ~25% for short exposures (10–30 s), while the main side reactions involve cleavage to glycine (yield 8%) and alanine (yield 10–15%), decarboxylation to phenylethylamine (yield 10–20%), and deamination to phenylpropionic acid (yield 10–20%). For longer exposures (1–20 min), the yields of phenylalanine and tyrosine decreased to ~15 and ~25% respectively.[94]

Since the single free carboxyl and the single free amino-group (which determine the occurrence of both side reactions and the amount of labile tritium) in peptides correspond to not one but several or even several tens of aminoacids residues, one can assume that peptides are more favourable (compared with aminoacids) objects for reaction with atomic tritium. Indeed, the peptide linkage in alanylalanine is not ruptured under TAM conditions,[101] while the fraction of labile tritium in labelled peptides is smaller by a factor of 3–5 than in the labelled aminoacids obtained under identical conditions[9] and the molar radioactivity of peptides is 100–1000 times greater than that of aminoacids.[92] Thus, under identical HFAM conditions, the labelled valine and the peptides containing it, namely Ile–Ile–Val and Phe–Ala–Ala–Val, have been obtained with radioactivities of 1.1, 0.2, and 2 c $mmol^{-1}$ respectively. The data for labelled peptides obtained by treatment with atomic tritium are compiled in Table 6.

Table 6.

Peptide	N	Method	a, Ci $mmol^{-1}$	φ, %	η, %	Refs.
Leu-Tyr-Leu	3	A	0.1	—	—	[10]
Ile-Ile-T-Val	3	A	0.2	—	—	[10]
Val-Ala-Ala-Phe	4	A	2.0	—	—	[10]
T-4 for a mixture obtained on hydrolysis of tobacco mosaic virus	7	B	0.2	—	—	[101]
Asp^1-Val^4-Angiotensin-II	8	C	0.3	40	—	[102]
Bradykinin	9	D	0.1	—	10	[9]
Angiotensin-I	10	E	0.4	32	2	[49, 66]
Gonadotropin releasing factor	10	F	2–3	—	—	[87]
Leuteinizing hormone-releasing factor (luliberin)	10	A	10.6	40	—	[103]
α-Amanitin		A	0.02	—	—	[76]
Somatostatin	14	A	0.75	—	—	[76]
T-8 from the products of hydrolysis of tobacco mosaic virus	20	B	2.8	—	—	[101]
Adrenocorticotropic hormone (ACTH)	39	A	10*	—	—	[76]
Antibiotic A-128	10	B	1–10*	—	—	[18]

Remarks. Method: A—HFAM (20 W, 2450 MHz, T_2 equivalent to ~1 Ci under circulation conditions, pressure 4 mmHg, 5 min), sample ≤10 mg; B—TAM (pressure ~0.01 mmHg, temperature of tungsten filament 2000 K, 2–5 min). The substance was deposited on the walls of a glass vessel cooled with liquid nitrogen; C—electric arc discharge, T_2 equivalent to ~6 Ci, pressure 10 mmHg, 30 min, sample 15 mg; D—HFAM (80 W, 40 MHz), 99 : 1 He–T_2 mixture, pressure 0.01 mmHg, sample 15 mg, E—TAM (T_2 equivalent to 0.03 Ci, pressure 0.01 mmHg, temperature of tungsten filament 2000 K, 0.5 min). The test substance was deposited on paper; F—HFAM (30 W, 2450 MHz, T_2 equivalent to 2 Ci under circulation conditions, pressure 4 mmHg, 15 min). The test substance (0.1–0.5 mg) was deposited on filter paper.

Notation: N is the number of aminoacid residues and φ and η are respectively the chemical and radiochemical yields.

*The biological activity was fully retained.

The aminoacid residues in peptides are labelled to different extents, which should be determined to a first approximation by the chemical structure of these residues. According to the results of model experiments with mixtures of 17 aminoacids, the probability of the introduction of tritium into non-labile positions in different aminoacids under TAM conditions (see Table 7)[20] decreases in the sequence aspartic acid ≥ serine > phenylalanine > tyrosine > cysteine > alanine, which is in general consistent with data for the reactions of atomic hydrogen with aminoacids in solution.[91] However, according to other data,[63,73] the sequence based on the decreasing reactivity of aminoacids under TAM conditions is different: alanine > cysteine > serine > aspartic acid. All these data apparently require revision.

The non-uniform incorporation of tritium into the aminoacid residues of peptides cannot apparently be explained solely with the aid of coefficients similar to those presented in Table 7. There is no doubt that the attack on the aminoacid

residue in the peptide is influenced both by the chemical nature of the neighbouring residues and by the steric structure of the peptide, which is indicated, in particular, by the different tritium contents in the like aminoacid residues in the T-4 and T-8 peptides from the hydrolytic reaction mixture obtained from the tobacco mosaic virus[20,101,104] (Table 6), while in the 20-membered T-8 peptide the deviation from the equi-probable distribution of tritium is significantly greater than in the shorter seven-membered T-4 peptide. Furthermore, the use of a mixture of aminoacids as a model is illegitimate, because the roles of the free amino- and carboxy-groups in the reactions of atomic tritium with both aminoacids and peptides are not comparable.

Table 7. The probability of the introduction of the label into various aminoacids (TAM conditions) per molecule (K) and per C–H bond (K') relative to alanine.

Aminoacid	K	K'	Amonoacid	K	K'
Alanine	1.00	0.33	Lysine	1.60	0.80
Arginine	1.19	0.60	Methionine	1.35	0.67
Aspartic acid	2.75	1.37	Isoleucine	1.48	1.48
Valine	1.72	1.72	Leucine	1.20	0.60
Histidine	1.76	0.88	Proline	1.39	0.70
Glycine	1.81	—	Serine	1.78	0.90
Gutamic acid	1.83	0.91	Tyrosine	1.08	0.54
Cysteine	1.04	0.52	Threonine	2.51	1.51
			Phenylalanine	1.20	0.60

Naturally in proteins the influence of steric factors should be manifested to an even greater extent and it has been suggested[72,105,106] that the very non-uniformity of the intermolecular distribution of tritium in the labelled proteins obtained on treatment with atomic tritium be used for the determination of the tertiary structure. In the case of the labelled sperm whale myoglobin, for example, the radioactivities of the valine-1 and valine-10 residues differed by a factor of 20,[101] and the residues with polar groups together with the N-terminal aminoacid proved most susceptible to attack by tritium atoms; on the other hand, the hydrophobic residues were labelled to a significantly smaller extent.[106] This is consistent with the generally accepted ideas concerning the preferential localisation of the polar aminoacid residues in the surface layer of the protein globule. The suitability, in principle, of the proposed method has been confirmed by X-ray diffraction data for different aminoacid residues in myoglobin although significant deviations have been observed for several residues.

Another application of labelled proteins obtained by treatment with atomic tritium is the determination of their primary structure.[76,101,105] Contrary to the previous case, here it is necessary that all the aminoacid residues should be labelled, i.e. that the label should be "total". It has therefore been suggested[101] that the proteins be denatured, before introducing tritium, by disrupting the order in their structure. Subsequent stepwise Edman degradation of the labelled protein leads to labelled aminoacid derivatives which can be determined in amounts of 0.1–10 nanomoles (depending on the value of a for the initial labelled protein).

Despite the interesting prospects for the investigation of the structure and functions of proteins with the aid of "totally" labelled compounds, hitherto the label has been introduced by treatment with atomic tritium into less than 20 proteins (Table 8); in a number of instances fairly high values of a have been achieved. For comparison, we may point out that labelled proteins with an almost total retention of their enzymic activity but with a only 0.001–0.015 Ci mmol^{-1} can be obtained by a modification of the Wilzbach method proposed recently (pressure ~0.1–35 mmHg, duration of exposure 1–60 h).[113]

Table 8. Labelled proteins.

Protein	Method	a, mCi mg^{-1}	a, m mmol^{-1}	Refs.
Bovine serum albumin	A	0.24	—	[72, 73, 107]
Ditto	B	0.005	—	[8]
"	C	0.1	—	[55]
Tobacco mosaic virus protein	A	—	1 000	[20]
γ-Globulin	D	—	—	[108]
Insulin	D	0.003–0.05	—	[109]
Collagen	A	—	540	[73]
β_2-Lactoglobulin	A	—	270	[73]
Lysozyme	D	1.0	—	[76]
Leuteinizing hormone	D	50	—	[10]
β_2-Microglobulin	D	0.5–5.0	—	[76]
Sperm whale myoglobin	A	—	4 000	[101, 106]
Ditto	D	0.5–1.0	—	[76]
Bovine pancreatic ribonuclease	A	—	500	[72, 73, 110]
Ditto	E	—	100	[9]
"	F	1000	—	[111]
Folic mulating hormone	D	50	—	[10]
α-Chymotrypsin	A	—	24 300	[72, 73]
Cyclo-AMP-dependent histone kinase	A	—	5 000	[112]

Remarks. Method: A—TAM (temperature of tungsten filament 2000 K, pressure 0.01 mmHg, 10–90 s), sample 2–5 mg; B—HFAM (T_2 equivalent to 0.05 Ci, 110 W, 90 s), sample ~20 mg; C—electric discharge (pressure 0.03–0.06 mmHg, 100 μA, 500 W, sample 0.5 g); D—HFAM (T_2 equivalent to 0.5–2 Ci, pressure 2–6 mmHg, 2450 MHz, 78 K, 5–20 min), sample 3–20 mg; E—HFAM (99:1 He–T_2 mixture, 40 MHz, 80 W, pressure 0.001 mmHg), sample ~5 mg; F—HFAM (T_2 equivalent to 10 Ci, pressure ~10 mmHg, 100 μA, 60 kW, 5 min (sample 50 mg).

Apparently further development of research involving labelled proteins, obtained by treatment with atomic tritium, is held back primarily by fears concerning side reactions which might take place during the introduction of the label and damage the structure and functions of the protein molecules. Such side reactions were already considered above for aminoacids and peptides; they are naturally possible also in the interaction of tritium atoms with proteins. Thus, when powdered aromatic aminoacid polymers as well as insulin, carboxypeptidase A, or papain were treated with hydrogen atoms generated under HFAM conditions, the radicals formed as a result of the addition of hydrogen atoms to the aromatic rings,[60,114] which can lead to the saturation of the latter, were identified (from the EPR spectra). The possible rupture of the sulphide bridges is a much greater risk for proteins than for peptides. The cleavage of proteins on application of the TAM has been observed in relation to bovine serum albumin.[107] However, in a number of other cases,[20,101,105,106] the bridges in polypeptides are not ruptured under TAM conditions.

The extent of all the side reactions indicated cannot be predicted *a priori* and can vary greatly for different proteins. On the other hand, the influence of the conditions used in the introduction of tritium on the retention of the native structure of the protein molecules has so far been investigated quite inadequately. All this shows how important it is to separate carefully the labelled native proteins from the products of side reactions. A general consideration of methods for the purification of proteins is outside the scope of the present review but affinity chromatography and, in particular, its variety, namely immunosorption, which has been used successfully in the purification of labelled ribonuclease[110] and serum albumin,[107] appear to be the most promising. The main advantage of these methods is their high specificity; furthermore, they make it possible to determine immediately the degree of retention of biological activity. We may note that, when the labelled protein does not lose its enzyme activity, the modification of some of the aminoacid residues in the course of the introduction of tritium does not prevent its employment in biological experiments, but such preparations are unsuitable for the study of the primary structure.

The difficulty of eliminating the products of side reactions makes another possibility of introducing the tritium label into proteins, namely with the aid of labelled modifying agents, extremely attractive. Many of these agents can be undoubtedly obtained successfully by treatment with atomic tritium. A good example is the labelled triethyloxonium tetrafluoroborate, mentioned above, whose radioactivity, when it is prepared with the aid of the TAM, can reach 5–6 Ci $mmol^{-1}$.[52,66] The use of this preparation for the esterification of terminal carboxyls makes it possible to obtain labelled modified proteins with a high radioactivity.

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Thus one may conclude that the thermal activation method is at present the most promising for the preparation of tritium-labelled compounds. Its universality, simplicity of application, low-consumption of tritium, and also the high levels of specific activities make it the most convenient for use in scientific organisations where radioisotope labels are employed in research. It is important to note in this connection that, using a simple apparatus, the investigator can himself introduce the label into the required preparation, including preparations of very complex structure, and obtain as a result a labelled product which is commercially unavailable. The method can be evidently easily converted into one of industrial importance and it may then find extensive applications in the isotope industry manufacturing tritium-labelled organic compounds.

From our point of view it is important to note yet another feature of the thermal activation method whereby it can be converted into a direct instrument for the study of the structures of micro-objects and macro-objects. Here we are dealing with the preferential localisation of the label in thin (3 – 10 Å) surface layers of the target due to the short free path of the reactive atoms. As a consequence, in analysing the distribution of tritium between the molecules constituting the given object or its intramolecular distribution, one can obtain a fairly clear and exact picture of the relative spatial dispostion of the fragments of the object. When applied to biological objects, this implies the possibility of investigating the topography of proteins in membranes and involved complexes (for example, nucleosomes), the steric organisation of biological macromolecules, etc. This application of the thermal activation method has already been shown to be promising and will undoubtedly develop.

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Institute of Chemical Physics,
USSR Academy of Sciences, Moscow

Shemyakin Institute of Bio-organic Chemistry, USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 1152-1171 (1984) U.D.C. 541.49

The Reactions of Carbene Complexes of Transition Metals with Unsaturated Hydrocarbons

A.I.Syatkovskii and B.D.Babitskii

The influence of the structure of individual carbene complexes of transition metals on the rates and stereoselectivities of their reactions with unsaturated hydrocarbons are examined.
The bibliography includes 114 references.

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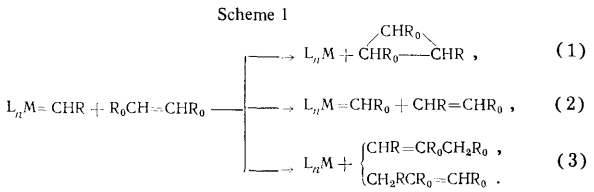
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I. INTRODUCTION

The carbene complexes of transition metals play a decisive role in complex catalytic processes involving the transformation of unsaturated hydrocarbons, such as the metathesis of cyclic and acyclic olefins,[1-6] the cometathesis of olefins with cyclopropanes,[7,8] and the polymerisation of alkynes,[9-11] and also in the formation of cyclopropanes from olefins on decomposition of aliphatic diazo-compound by transition metal salts.[12-15] The catalysts of these processes are as a rule multicomponent systems in which it is extremely difficult to determine the specific parameters of the active centres formed (the degree of oxidation of the metal, its ligand environment, the characteristics of the carbene ligand, etc.). The lack of such information significantly hinders the study of the reaction mechanism and hence prevents a purposeful search for more effective and stereoselective catalytic systems. On the other hand, the considerable progress achieved in the synthesis of a whole series of individual carbene complexes of transition metals, capable of reacting with unsaturated hydrocarbons or cyclopropanes, makes it possible to regard them as adequate models of the active centres in the catalytic processes enumerated above.

Depending on the nucleophilicity or the electrophilicity of the carbene ligand, the reactions of the carbene complexes with olefins can proceed via the following pathways; the conversion of the olefin into a cyclopropane derivative (1), the exchange of alkylidene fragments between the olefin molecule and the carbene complexes (2), and the addition of the carbene ligand to the olefin with formation of a set of new olefins (3):

Scheme 1

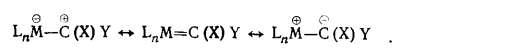


The aim of the present review is to discuss the influence of the structures of different carbene complexes on the rates and stereoselectivities of their reactions with olefins. We believe that it is useful to carry out such a survey because the existing reviews on the chemistry of carbene complexes of transition metals are devoted either to electrophilic[16-22] or nucleophilic[23] complexes which naturally precludes the analysis of reactions (1)-(3) from a single standpoint. Furthermore, in the communications enumerated above attention was concentrated on relatively stable carbene complexes for which reactions with unsaturated hydrocarbons are in general uncharacteristic.

This review deals with the reactions of only individual carbene complexes of transition metals and is not concerned with the problems associated with the possible mechanisms of the generation and role of such complexes in catalytic processes.

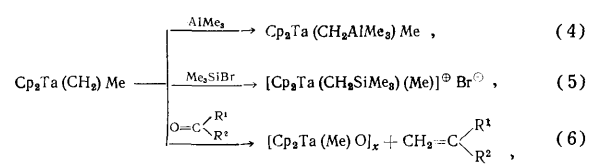
II. THE METAL–CARBON BOND IN ELECTROPHILIC AND NUCLEOPHILIC CARBENE COMPLEXES OF TRANSITION METALS

X-Ray diffraction and spectroscopic data have shown that in mononuclear complexes of the type $L_nM{=}C(X)Y$ (I) the carbene carbon is sp^2-hybridised, while the M, C, X, and Y atoms are usually located in a single plane.[16-23] The conventional subdivision of carbene complexes in terms of their chemical reactions into electrophilic and nucleophilic involves the consideration of a specific molecule in terms of the predominant contribution of the three possible resonance structures (II)-(IV):



(II) (III) (IV)

For example, the carbene ligand in the tantalum and niobium complexes enters into typical nucleophilic reactions and such complexes have come to be described in terms of the resonance structures (III) and (IV):[23-26]



Here



In the chemical reactions represented by Eqns.(4)–(6) the nucleophilic carbene complexes behave as analogues of ylides, such as, for example, the phosphonium ylides $R_3\overset{+}{P}-\overset{-}{C}H_2$ (where R = alkyl or aryl). Indeed reactions (4) to (6) can be compared with the analogous reactions of phosphonium ylides (the formation of adducts with electron-deficient boron and aluminium compounds, alkylation of ylides with formation of phosphonium salts, and the Wittig reaction respectively).[27]

In contrast to the tantalum complexes examined above, the pentacarbonylcarbene complexes of chromium, molybdenum, tungsten and also certain complexes of iron and rhenium react in conformity with the resonance structures (II) and (III).[28–31]

In electrophilic carbene complexes the attack by nucleophiles is on the carbene carbon atom and reactions (8)–(11) are to some extent similar to the reactions known for individual singlet carbenes†: the formation of ylides in the reactions with phosphines and amines, insertion in the metal–carbon bond, and the carbene–olefin isomerisation:[12,32,33]

$$(CO)_5W[C(OMe)Ph] \xrightarrow{LiPh} Li^{\oplus}\{(CO)_5W^{\ominus}-[C(Ph)_2OMe]\}, \quad (8)$$

$$(CO)_5W(CHPh) \xrightarrow{PPh_3} (CO)_5W[C(H)(Ph)(\overset{\oplus}{P}Ph_3)], \quad (9)$$

$$[Cp(PPh_3)(NO)Re(CH_3)]^{\oplus} \xrightarrow{C_5H_5N} [Cp(PPh_3)(NO)Re(CH_2\cdot C_5H_5N)]^{\oplus}, \quad (10)$$

$$(CO)_5W[C(Me)Ph] \xrightarrow{\Delta} (CO)_5W[CH_2{=}CHPh]. \quad (11)$$

The phenomenological approach to the reactions of carbene complexes examined above is in many instances inapplicable despite its attractive simplicity. For example, it is obscure within the framework of this approach why the carbene ligand linked to an 18-electron centre in the complexes $(CO)_5W(CHPh)$, $(CO)_5Cr[C(OMe)Me]$, or $[Cp(CO)_2Fe(CH_2)]^+$ undergoes electrophilic reactions, while in the electron-deficient complexes of tantalum $Cl_2CpTa(CHCMe_3)$ and $Cp(PMe_3)_2(C_2H_4)Ta.(CHCMe_3)$ containing 14 and 16 electrons respectively in the valence shell of the transition metal the carbene species enters into nucleophilic reactions.[34] The treatment of nucleophilic carbene complexes as analogues of phosphonium ylides is particularly unsatisfactory, because these compounds react similarly only with fairly polar reagents (see Section IV). Furthermore, the representation of the carbene complexes by formulae (II)–(IV) makes it impossible to infer the strength with which the carbene is bound to the transition metal, which is one of the most important factors in the determination of the reaction pathway. For a correct interpretation of the reactivity of carbene complexes, it is necessary to analyse the nature of the bond between the transition metal and the carbene species.

The results of quantum-chemical calculations on carbene complexes by non-empirical[35,36] and semi-empirical[34,37,38] methods have shown that the carbene ligand is bound in the complex mainly as a result of the transfer of electrons from the σ orbital of the carbene carbon to the metal (σ-binding) and the reverse transfer of electron density from the highest occupied molecular orbital (HOMO) of the metal with the corresponding symmetry to the unoccupied $2p_z$ orbital of the carbene (π-binding).

In conformity with the perturbation theory, one can predict that the efficiency of the π-binding is determined by two factors. It is directly proportional to the square of the overlap integral between the HOMO of the metal and $2p_z$ orbital of the carbene and is inversely proportional to the difference between the energies of these orbitals.[34] Calculations for model methylene complexes of chromium, iron, and tantalum have shown that both factors promote the most effective π-binding in the case of tantalum, for which the highest population of the $2p_z$ orbital of the carbene ligand has been obtained.[34]

On the other hand, a semiempirical calculation for the $(CO)_5Cr[C(Me)OMe]$ molecule[37] and the experimental study of the EPR spectra of the radical-anions obtained on chemical reduction of this and similar complexes[39] show that in these compounds the lowest unoccupied molecular orbital (LUMO) of the complexes is almost entirely the $2p_z$ orbital of the carbene fragment, i.e. the π-binding in these complexes is minimal.

Thus the increase of the effectiveness of the π-binding increases the population of the $2p_z$ orbital of the carbene ligand and hence increases its nucleophilicity. Furthermore, an increase of the effectiveness of the π-binding is equivalent to an increase of the amount of double bond character of the linkage between the metal and the carbene carbon and should therefore be reflected in parameters such as the metal–carbon bond strength and the energy barrier to the rotation of the carbene around this bond in the complex. Experimental data permitting a comparison of the strengths of the metal–carbon bonds in electrophilic and nucleophilic carbene complexes are unfortunately lacking but nevertheless attention should be drawn to the fact that nucleophilic methylene, benzylidene, and neopentylidene complexes of tantalum are more stable in reactions involving the transfer of the carbene ligand than the corresponding electrophilic complexes of tungsten or iron. The possibility of the rotation of the carbene species around the metal–carbon bond in the complex has been studied experimentally[40–46] and with the aid of quantum-chemical calculations.[36,38,47,48] Apparently an increase of the nucleophilicity of the carbene ligand does indeed lead to an increase of the activation energy for rotation although even a semiquantitative estimate of the relative contributions of the electronic and steric interactions to the rotation barrier involves enormous difficulties.

The electron distribution in the carbene ligand and hence its reactivity depend also on the substituents attached to the carbene carbon. For electrophilic complexes, the influence of the nature of α-substituents at the carbene carbon atom on its reactivity can be illustrated by comparing different pentacarbonyl carbene Fischer complexes:

$$(CO)_5M{=}C\begin{matrix}ZR\\ \diagdown\\ R'\end{matrix} \quad (V)$$

where Z = O, N, or S, M = Cr, Mo, or W, and R, R' = alkyl or aryl.

In complexes (V) the presence of substituents capable of behaving as π-donors in the α-position relative to the carbene carbon leads to the transfer of electron density from the ZR group to the $2p_z$ orbital of the carbene, which is responsible for the appearance of partial double bond character in the linkage between the C_{carb} and Z atoms.[16–22] {An analogous effect has been observed also for the compound $[Cp(CO)_2Fe(CHPh)]^+$ and the existence of conjugation between the benzene ring and the carbene carbon in this complex has been demonstrated.[49]} The carbene ligand in the Fischer complexes remains an electrophilic centre, although the capacity of such complexes for reactions with nucleophiles is lower than that of the complexes $(CO)_5W(CHPh)$ and $(CO)_5W(CPh_2)$ which have a similar structure.[19,21,30,50,51]

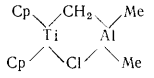
†The term singlet carbene is used to designate carbene species with zero spin regardless of whether in terms of free energy this is the ground state (CF_2; CCl_2) or the first excited state (CH_2; CHCOOMe).

The transfer of electron density to the carbene carbon in the complex $\{Cp(CO)(PPh_3)Fe[C(Me)OEt]\}^+$ is so great that the complex can react with nucleophiles as a carboxonium salt:[52]

$$\left[Cp(CO)(PPh_3)Fe{-}C(Me)(\overset{\oplus}{O}Et)\right] + I^{\ominus} \rightarrow EtI + Cp(CO)(PPh_3)Fe{-}C(Me)(O) \quad .$$

There are very few data concerning the influence of the substituents at the carbene carbon atom on the reactions of nucleophilic carbene complexes. It has been established[53,54] that, for a fixed ligand environment, the methylene, neopentylidene, and benzylidene complexes of tantalum and niobium differ only in the rate of addition of the carbene ligand to olefins, while the replacement of the ligands in the coordination sphere of the metal is reflected both in the rate of the reaction and in its regioselectivity (Section IV).

In discussing the influence of the substituents at the carbene carbon atom on the reactivity of the carbene complexes, it is necessary to note the existence of a group of nucleophilic complexes in which a kind of stabilisation of the carbene ligand is achieved as a result of the formation of adducts with organoaluminium compounds.[55-58] Among compounds of this kind, the methylene complex of titanium having the structure



(VI)

was studied in greatest detail.[55-57] The carbene ligand in these dinuclear complexes is of the bridge type and manifests nucleophilic properties in its reactions.[55,56] Complexes of type (VI) will be considered in Section IV.

The data described indicate that the nature of the transition metal and its ligand environment determine mainly the nucleophilic or electrophilic character of the chemical reactions of the carbene ligand in the complex, while the substituents in the α-position relative to the carbon atom influence only the relative reactivity without altering as a rule the overall reaction pathway.

In conclusion of this Section we shall return to the question of the legitimacy of representing the carbene complexes of transition metals by the resonance formulae (II)–(IV). The low barrier to rotation about the metal–carbon bond and the considerable polarisation of the latter as a result of the effective transfer of electron density to the metal atom (σ-binding) make it possible to describe fairly correctly the electrophilic carbene complexes by the resonance structure (II). In the nucleophilic carbene complexes the metal–carbon bond is formed as a result of two processes: the transfer of electron density to the metal (σ-binding) and the reverse transfer of electron density to the $2p_z$ orbital of the carbene ligand (π-binding). One can therefore assume that the distribution of electron density in the carbene ligand resembles that in a triplet carbene with a partly filled $2p_z$ orbital rather than distribution in a carbanion (as in phosphonium ylides[59,60]). Such biphilicity is manifested, in particular, in the ability of the carbene ligand in nucleophilic carbene complexes to interact effectively with the π-electron system in olefins (Section IV). Thus the description of nucleophilic complexes by formula (IV) is not entirely correct.

III. THE REACTIONS OF ELECTROPHILIC CARBENE COMPLEXES

Conversion into cyclopropane derivatives is the most typical reaction of the electrophilic carbene complexes with olefins. Like the reactions of free singlet carbenes with olefins, the process proceeds *cis*-stereospecifically.[18-21,29,61,62] Scheme 2 presents the products of the reactions of the benzylidene complexes of iron[62] and tungsten[29,61] with *cis*- and *trans*-but-2-enes and α-olefins;

Scheme 2

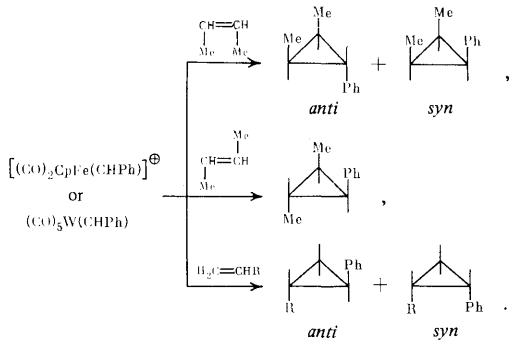


Table 1. The ratio of the *syn*- and *anti*-isomers of cyclopropanes produced in the reactions of $(CO)_5W(CHPh)$ [61] and $[Cp(CO)_2Fe(CHPh)]^+$ [62] with various olefins.

Olefins	$(CO)_5W(CHPh)$	$[Cp(CO)_2Fe(CHPh)]^{\oplus}$
Propene	1.8	7.8
But-1-ene	0.9	6.5
3-Methylbut-1-ene	0.36	4.6
Styrene	9.7	⩾100
cis-But-2-ene	41	>100
Cyclopentene	2.6	⩾200
2-Methylbut-2-ene	94	>50

During the process, there is no preliminary "ejection" of the carbene from the complex and, at least in the stage determining the stereoselectivity of the addition, the carbene remains bound to the transition metal.[18,21,63] The reactivity of the complexes, determined by the electrophilicity of the carbene ligand, varies within wide limits for different compounds. The most reactive complexes are those in which the carbene ligand contains no heteroatoms in the α-position relative to the carbene carbon: $(CO)_5W(CHPh)$, $[Cp(CO)(PPh_3)Fe(CHMe)]^+$, $[Cp(CO)_2Fe(CHPh)]^+$, $[Cp(CO)_2Fe(CH_2)]^+$, etc. Even at −70 °C these complexes enable the corresponding cyclopropanes to be obtained from olefins in high yields.

The study of the reactions of the complex $[Cp(CO)_2Fe(CH_2)]^+$ with olefins showed that olefins containing an electron-rich double bond of the type of that in ethyl vinyl ether are more reactive than but-1-ene or cyclohexene.[41] The relative reactivity series for olefins in the reaction with the complex $(CO)_5W(CHPh)$ has been obtained[61] and a satisfactory correlation has been observed with the analogous series for the reaction involving the formation of cyclopropane by free carbenes in the singlet state:[64,65]

$$\underset{\sim 0}{CH_2{=}CH_2} \ll \underset{1.0}{CH_2{=}CHCMe_3} < \underset{10.9}{CH_2{=}CHMe} \sim \underset{7.6}{MeCH{=}CHMe} \ll \underset{850}{MeCH{=}CMe_2} \ll \underset{3500}{CH_2{=}CMe_2} \quad . \qquad (12)$$

The observed reactivity series for olefins shows that the rate of addition of the carbene ligand is determined in the first place by the charge on the most substituted carbon atom

in the olefin. This suggests that, in the transition state arising during the conversion of olefins into cyclopropanes by complexes of the type $(CO)_5W(CHPh)$, charge separation should take place, the excess positive charge being stabilised by the alkyl substituents at the most substituted carbon atom.[61] All these results not only emphasise the electrophilic character of the carbene ligand in the cyclopropane formation reaction but also reveal the similarity of the mechanisms of the reactions of electrophilic carbene complexes and free singlet carbenes with olefins.

When there are no coordination vacancies in the electrophilic complex at the metal atom, the LUMO of the complex is localised at the carbene ligand. The interaction of this complex with an olefin apparently proceeds analogously to the interaction of singlet carbenes with olefins—as electrophilic attack by the unoccupied $2p_z$ orbital of the carbene on the π-electron system of the olefin with formation of cyclopropanes.[66,67]

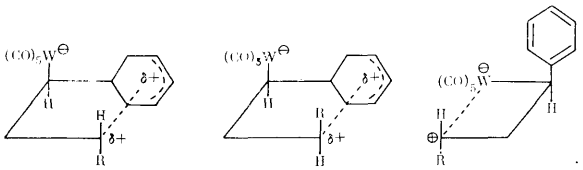
More detailed information about the mechanism of the interaction of the electrophilic complexes with olefins is provided by the study of the influence of the nature of the reactants on the ratio of the *syn*- and *anti*-isomers in cyclopropanes—the reaction products (Scheme 2). Certain results have been taken from the literature[61,62] and are presented in Table 1, which shows that the iron complex gives rise in all cases to higher ratios of the *syn*- and *anti*-isomers of cyclopropanes, but the character of the variation of the stereoselectivity as a function of the structure of the olefin is identical for the two complexes studied. Furthermore, it is possible to identify the following features:

(a) among the products of the interaction of olefins with the above complexes the thermodynamically unfavourable *syn*-isomer is formed predominantly in most cases;

(b) an increase of the steric volume of the alkyl substituents at the double bond in α-olefins decreases the fraction of the *syn*-isomer.

In order to explain the results, a mechanism has been proposed[61] involving the possibility of the stabilisation of the positive charge in the intermediates (VII) and (VIII) by the π-electron system of the benzene ring; the intermediate (VII), leading to the formation of the *syn*-isomer, is energetically more favourable than the intermediate (VIII), since there is no steric repulsion between the R and $W(CO)_5$ groups in it.

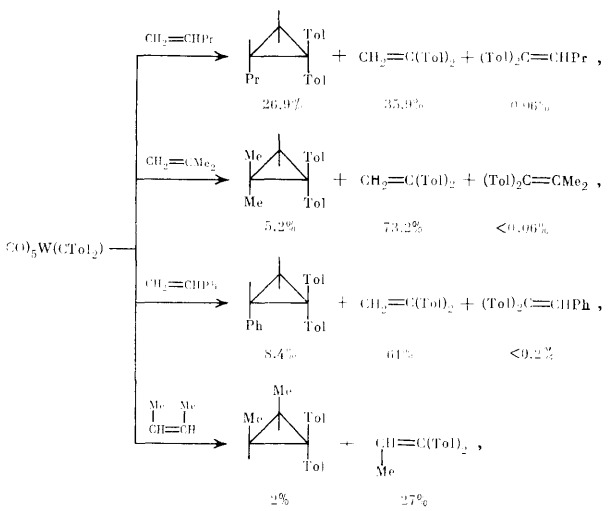
An increase of the steric volume of the substituent R in the olefin decreases the role of the stabilisation by the π-electrons of the benzene ring and the process can proceed via intermediates of type (IX) whose formation is controlled by the difference between the free energies of the reaction products.



(VII) (VIII) (IX)

Experimental confirmation of this hypothesis has been obtained.[62] It has been shown that, on passing from $[Cp(CO)_2Fe(CHPh)]^+$ to the complex $\{Cp(CO)_2Fe[C(H).(p\text{-}CH_3C_6H_4)]\}^+$, which has an electron-donating substituent in the ring, the ratio of the *syn*- and *anti*-isomers in the products of addition to propene increases from 7.8 to 10.0. It is noteworthy that the concept of the stabilisation of the positive charge in the transition state in the cyclopropane formation reaction by the benzene ring had been put forward earlier by Closs and Moss to account for the tendency towards the preferential formation of the *syn*-isomers in the reactions of phenylcarbenes, generated in different ways, with but-1-ene, *cis*-but-2-ene, and 2-methylbut-2-ene.[68-70] Other factors promoting the formation of the *syn*-isomer can probably also exist. It has been established that the reactions of $[Cp(CO)_2Fe(CHMe)]^+$ with styrenes and cyclo-octene result in the formation of cyclopropanes in which the ratios of the *syn*- and *anti*-isomers are 4.7 and >4.5 respectively.[46] On the basis of the analogy with the reactions of free singlet carbenes, one can assume, for example, that the *syn*-disposition of the substituents in the transition state (or the intermediates) favours a more effective charge transfer from the HOMO of the olefin to the LUMO of the carbene.[66,71,72]

If the electrophilicity of the carbene ligand in the complex is reduced as a result of the substituents in the α-position relative to the carbene carbon [this is characteristic, for example, of the Fischer complexes (V)], then its reactivity in relation to olefins diminishes. The dissociation of the metal–carbon bond in such complexes and the transfer of the carbene ligand to the olefin take place at temperatures above 50 °C.[18-21,30,51] However, at the temperatures indicated it is necessary to reckon with the dissociation of the initial compound to form CO and a coordination-unsaturated carbene complex,[19,21,61,73] which leads to a new pathway in the reactions with olefins. Thus ditolylcarbenepentacarbonyltungsten (X) reacts with olefins at ~70 °C to form cyclopropanes and the products of the exchange of the alkylidene fragments.[51,74]



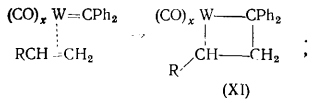
where Tol = *p*-Me–C_6H_4.

The following series of relative reactivities of olefins in relation to complex (X) has been established:[74]

$$\underset{49.5}{CH_2{=}CHPr} > \underset{10.4}{CH_2{=}CMe_2} > \underset{1.0}{MeCH{=}CHMe} > \underset{\sim 0}{MeCH{=}CMe_2}\ .$$

To a first approximation, this series agrees with the relative thermodynamic stabilities of transition metal complexes of olefins[75] but is the reverse of series (12) of the relative reactivities of olefins in the reactions with $(CO)_5W(CHPh)$.

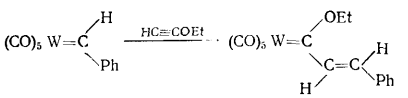
The experimental data obtained agree best with the following scheme: owing to the dissociation of the initial complex during the reaction, a coordination vacancy appears at the metal atom and the reaction with olefins can proceed via a metallacyclobutane intermediate of type (XI):



(XI)

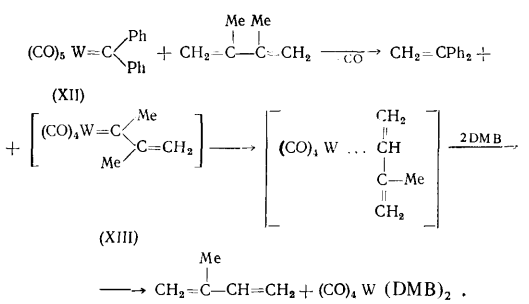
its decomposition in fact leads to the formation of the products of the exchange of alkylidene fragments. Later studies showed that the ratio of the products of the transalkylidenation reaction and the cyclopropanes in the reactions of compound (X) with olefins is independent of the carbon monoxide pressure in the system[73] and cyclopropanes are apparently formed in this instance also via the intermediate (XI). The possibility of the preliminary abstraction of one of the CO groups in the carbene complex apparently arises also in the reactions of the Fischer complexes (V) with olefins containing electron-accepting groups.[21]

Electrophilic carbene complexes can react with acetylenes,[61] dienes,[76,77] and cyclopropanes[78] and the above compounds behave similarly to olefins. For example, the complex $(CO)_5W(CHPh)$ enters into the transalkylidenation reaction with ethoxyacetylene, which behaves as a cyclo-olefin with a ring of "zero" size:[61]



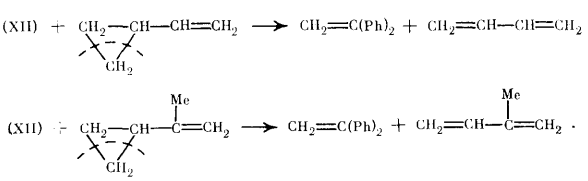
The complexes $(CO)_5W(CPh_2)$ and $(CO)_5W[C(Me)Ph]$ react analogously with ethoxyacetylene.

Diphenylcarbenepentacarbonyltungsten (XII) reacts with 2,3-dimethylbuta-1,3-diene (DMB) in accordance with the following scheme:[76,77]



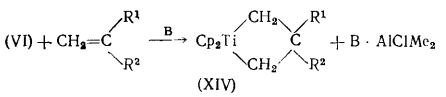
(XIII)

In the first stage the alkylidene fragments are exchanged between complex (XII) and DMB, which results in the formation of 1,1-diphenylethylene and the carbene complex (XIII). The second stage of the reaction consists of the carbene–olefin isomerisation in the intermediate carbene complex (XIII) with formation of an isoprene molecule [cf. Eqn.(11)]. At ~90 °C the same complex (XII) is capable of demethylenating three-membered carbon rings,[78] which can be regarded as a kind of metathesis reaction of cyclopropanes:[7,8,79]



IV. THE REACTIONS OF NUCLEOPHILIC CARBENE COMPLEXES

The difference in the nature of the carbene species in nucleophilic complexes with transition metals and in complexes with phosphines is manifested most clearly in the reactions with olefins having a non-polarised or a weakly polarised double bond. Phosphonium ylides do not react with such olefins, whereas two reaction pathways have been observed for nucleophilic carbene complexes: the exchange of the alkylidene fragments (2) and the addition of the carbene ligand to the olefin with formation of new olefins (3). It has been suggested that both these reactions proceed via a four-centre transition state with formation of intermediates of the metallacyclobutane type. Sometimes it is possible to isolate and characterise such a metallacyclobutane (XIV):[80,81]



(13)

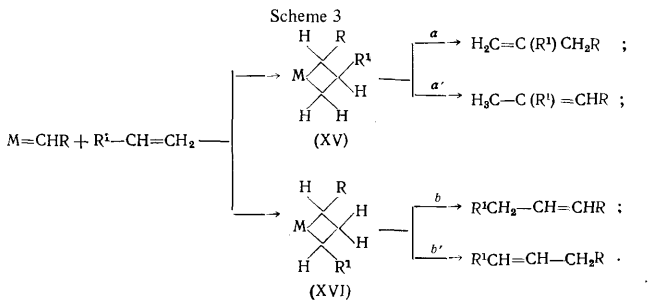
(XIV)

R^1 = t-Bu, R^2 = H; R^1 = iso-Pr, R^2 = H; R^1 = Ph, R^2 = H; $R^1 = R^2$ = H; $R^1 = R^2$ = Me; B = Lewis base.

As a rule, the metallacyclobutane formed decomposes rapidly and its structure can be inferred only on the basis of the reaction products.

Electron-deficient nucleophilic complexes of tantalum and niobium react with α-olefins to form a set of new olefins.[23,53,54,82–84] A reaction of this type has been studied in greatest detail for the tetrahedral complex $CpCl_2Ta(CHCMe_3)$ [83,84] and also for several octahedral complexes of tantalum and niobium having the general formulae $L_2Cl_3M(CHCMe_3)$ and $L_2Cl_3M(CHPh)$, where M = Ta or Nb and L = PPh_3, PPh_2Me, or $PPhMe_2$.[53,54] Four different olefins can be formed in the general case as a result of the reaction:

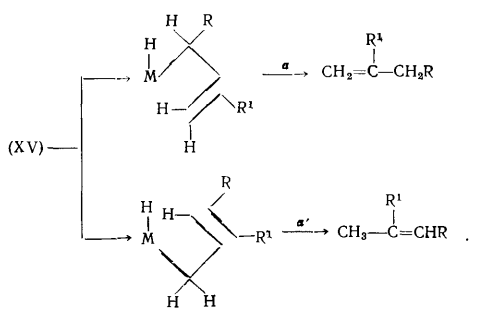
Scheme 3



(XV) (XVI)

The ratios of the olefins depend on the structure of the carbene complex and the olefin (Table 2).

The reaction products *a*, *a'*, *b*, and *b'* are formed as a result of β-elimination in the metallacyclobutanes (XV) and (XVI) with subsequent addition of a proton to the α- or α'-position in the metalla-ring.[54,82–84] For example, products *a* and *a'* are formed as follows in the decomposition of the metallacyclobutane intermediate (XV):



(14)

The ratio of the contributions of the pathways $(a + a')/(b + b')$ depends only slightly on the initial carbene complex and the olefin, which indicates the absence of an explicit preference for the formation of the intermediate (XV) or (XVI). Thus

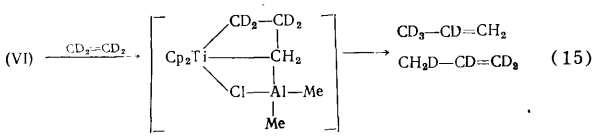
the hypothesis, put forward initially by McLain and co-workers,[82-84] that the polarisation of the metal–carbon bond in the carbene complexes of tantalum and niobium has a decisive influence on the regioselectivity of their reactions with α-olefins has not been confirmed.

Table 2. Composition of the products of the reactions (as percentages) of the neopentylidene and benzylidene complexes of tantalum with ethylene, propene, and styrene.[54]

Olefin	*a*	*a'*	*b*	*b'*
	$(PMe_3)_2Cl_3Ta(CHPh)$			
Ethylene	—	—	73	27
Propene	49	21	4	26
Styrene	5	49	46	
	$(PMe_3)_2Cl_3Ta(CHCMe_3)$			
Ethylene	—	—	7	93
Propene	8	42	7	43
Styrene	6	35	30	29

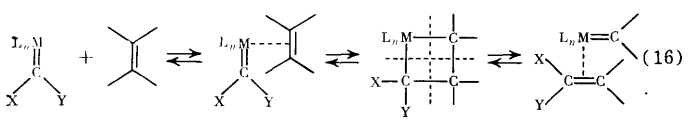
Note. Pathways *a* and *b'* and also pathways *a'* and *b* are equivalent for ethylene.

The reaction involving the transfer of the carbene ligand to ethylene with formation of new olefins has also been observed for complex (VI)[55,56] and the distribution of the deuterium label in the reaction products supports the following reaction mechanism:

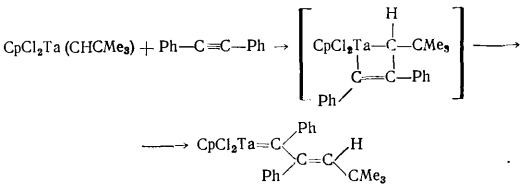


(15)

If the pathway, discussed above, leading to the decomposition of the metallacyclobutane intermediate via β-elimination is ineffective (the simplest case obtains when there are no protons at the β-carbon atom), then the metallacyclobutane formed can again decompose reversibly into a metal–carbene-olefine complex. The decomposition of the metallacyclobutane can proceed in principle in two ways, which leads to the possibility of the exchange of alkylidene fragments between the transition metal and the olefin:


(16)

For example, it has been established that complex (VI), which effects the irreversible transfer of the methylene ligand to ethylene [reaction (15)] on interaction with isobutene or methylene cyclohexane, exchanges the methylene group with these olefins. If a mixture of isobutene and labelled [^{13}C]methylenecyclohexane is used, then in the presence of complex (VI) the label is distributed between both olefins.[56,57] Another example involves the carbene complex $CpCl_2Ta(CHCMe_3)$, which reacts with ethylene or styrene exclusively in accordance with Eqn.(3). On interaction with diphenylacetylene, the complex gives rise to a kind of transalkylidenation reaction, which proceeds via a metallacyclobutane intermediate:[23,84]:



The absence of protons at the β-carbon atom in the metallacyclobutane intermediate is the simplest but not the only factor promoting the transalkylidenation reaction. It is known that, by altering the ligand environment of the metal atom in the complex, it is possible to influence the effectiveness of the β-elimination reaction.[85] It has been shown[54,86] that the relative reactivity in the β-elimination of hydrogen in alkyl compounds of tantalum and niobium is reduced when ligands such as tetrahydrofuran, pyridine, or alkoxy-groups are present in the coordination sphere of the metal, the effect being particularly pronounced in the last instance.

The introduction of the ligands enumerated above into the coordination sphere of the carbene complexes of niobium and tantalum reduces the relative rate of decomposition of the metallacyclobutane intermediate via β-elimination, which increases the yield of the products of the transalkylidenation reaction:[53,54]

$$\underset{\text{(XVII)}}{(PMe_3)_2Cl_3Nb(CHCMe_3)} + CH_2{=}CH_2 \rightarrow \underset{7\%}{CH_2{=}CHCH_2CMe_3} + \underset{93\%}{Me{-}CH{=}CH{-}CMe_3} \quad (17)$$

$$\underset{\text{(XVIII)}}{(THF)_2Cl_3Nb(CHCMe_3)} + CH_2{=}CHEt \rightarrow \underset{73\%}{CH_2{=}CHCMe_3} + \begin{cases} Pr{-}CH{=}CH{-}CMe_3 \\ Et{-}CH{=}CH{-}CH_2CMe_3 \end{cases}\ \underset{17\%}{} \quad (18)$$

$$\underset{\text{(XIX)}}{(PMe_3)(OCMe_3)_2ClNb(CHCMe_3)} + CH_2{=}CHEt \rightarrow \underset{86\%}{CH_2{=}CHCMe_3} + \underset{6\%}{Me_3CCH{=}CHEt} \quad (19)$$

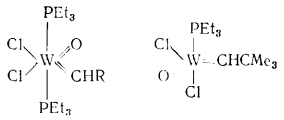
It follows from Eqns.(17)–(19)# that the reaction of complex (XVII)with ethylene proceeds as the transfer of the carbene ligand to the olefin with formation of a set of new olefins, while complex (XIX) undergoes highly selectively the transalkylidenation reaction with t-butoxy-groups: complex (XVIII) is an example of a compound capable of reacting with olefins via both pathways simultaneously. An analogous effect has also been observed for tantalum complexes.[53,54]

The study of the composition of the products of the reactions of neopentylidene complexes of niobium and tantalum with but-1-ene and *cis*-pent-2-ene showed that the relative contribution of the transalkylidenation reaction is greater in the second case.[54] The results obtained suggest that the β-elimination reaction is more probable for α,α'-substituted metallacyclobutanes than for the α,β,α'-substituted derivatives.

Some of the complexes discussed above are capable not only of transferring the initial carbene ligand but also of propagating the kinetic chain in the metathesis reaction. For example, in the metathesis of *cis*-pent-2-ene in the presence of the complex $(PMe_3)Cl(OCMe_3)_2.Nb(CHCMe_3)$, 29 equivalents of but-2-ene and 34 equivalents of hex-3-ene are formed in 24 h per equivalent of the complex. At the same time effective *cis–trans* isomerisation of the initial *cis*-pent-2-ene takes place until the attainment of the composition corresponding to thermodynamic equilibrium.[54]

#Only the main products of the reactions of the initial neopentylidene complexes with olefins are presented in Eqns.(17)–(19).[54]

The formation of the products of the β-elimination of metallacyclobutanes in the course of the reaction with olefins has been observed to some extent for all the carbene complexes of niobium or tantalum (with the exception of the complexes containing the t-butoxy-ligands[53,54]) and for this reason the nucleophilic oxoalkylidene complexes of tungsten (XX) and (XXI), which react with olefins exclusively via the metathesis pathway, are of very great interest:[53,87,88]



(XX) (XXI)

R=H(a); Me(b); Et(c); Ph(d); or CMe_3(e).

According to the data of Wengrovius et al.,[87] complexes (XX) interact with olefins fairly slowly, but their reactivity in the transalkylidenation reaction can be significantly increased by introducing Lewis acid such as $AlCl_3$, $AlEtCl_2$, $SnCl_2$, etc. as additives to the reaction medium. Complex (XXI) is reactive also in the absence of additives and the initial rate of the transalkylidenation of olefins in the presence of complex (XXI) is equal to the initial rate of the same reaction in the presence of the catalytic system (XXe) + $AlCl_3$.[87] This enabled the authors to postulate that complex (XXI) behaves as an active centre, which effects transalkylidenation also in the (XXe) + $AlCl_3$ binary systems§.

In the reactions of complex (XX) and (XXI) with olefins, it is possible to characterise not only the olefins produced as a result of the transfer of alkylidene fragments but also the carbene complexes formed in the course of the transalkylidenation. For example, the interaction of the neopentylidene complex (XXe) with *cis*-pent-2-ene leads to the formation of approximately equivalent amounts of 2,2′-dimethylhex-3-ene and 4,4′-dimethylpent-2-ene and the corresponding carbene complexes (XXb) and (XXc). On the other hand, in the reaction of complex (XXe) with but-1-ene the only product of the transalkylidenation reaction of the initial complex is 3,3′-dimethylbut-1-ene, while the other possible product, namely 2,2′-dimethylhex-3-ene, was not detected.[87]

The cyclopropane formation reaction, which is most characteristic of electrophilic carbene complexes, has not been observed for nucleophilic carbene complexes of tantalum, niobium, or tungsten. Only one example of the cyclopropane formation reaction is known for the nucleophilic complexes, namely the titanium complex (VI) reacts with isobutene to form 1,1′-dimethylcyclopropane in ~2% yield.[55] It has been established that the fraction of cyclopropanes formed in this reaction increases in the following sequence: ethylene < propene < isobutene; it also increases with the polarity of the solvent employed. A similar reactivity series has been observed for the reactions of electrophilic complexes with olefins [reactions (12)]. It is therefore possible to postulate that the cyclopropane formation reaction involving the titanium complex (VI) proceeds without the formation of a metallocyclobutane intermediate. The fact that the individual compounds $Cp_2\overline{Ti-CH_2-CHR-CH_2}$ (R = t-Bu or iso-Br) do not yield even traces of cyclopropane on decomposition can serve as confirmation of this hypothesis.[80] It is noteworthy that the absence of cyclopropanes from the products of the reactions of nucleophilic carbene complexes with olefins does not imply that this pathway in the decomposition of metallacyclobutanes is in principle impossible (see SectionV).

V, THE PATHWAYS IN THE REACTIONS OF CARBENE COMPLEXES OF TRANSITION METALS WITH OLEFINS

Comparison of the reactions of free carbenes and the carbene complexes of transition metals with olefins shows that complex formation not only alters the reactivity of the carbene species but also leads to the appearance of two new reaction pathways: transalkylidenation (2) and the addition of the carbene to the olefin with formation of new olefins (3). The appearance of these specific reactions, which are not characteristic of free carbenes, has been attributed to the ability of the transition metal atom in the carbene complex to coordinate an olefin molecule with subsequent formation of a metallacyclobutane intermediate [reaction (15)].

The results of Hoffmann's semiempirical calculations show that the energy barrier to the formation of metallacyclobutanes¶ from the carbene complex and an olefin is reduced with increase of the positive charge on the metal.[89] This conclusion agrees well with the experimental finding that metallacyclobutane intermediates are formed preferentially precisely in the interaction of nucleophilic carbene complexes with olefins (see Section IV).

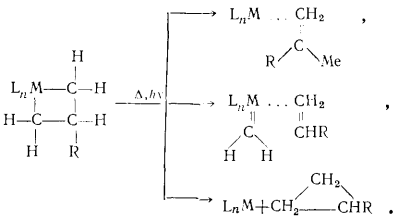
The energy profile of reaction (16) of certain methylene complexes of chromium, molybdenum, tungsten, and titanium with ethylene has been calculated non-empirically.[35,90,91] The free energy of formation of the metallacyclobutane ΔG for the compound $Cl_2Ti(CH_2)$ is -34.5 kcal mol^{-1},[90] which agrees well with the formation of stable metallacyclobutanes (XIV) in the reaction of the titanium complex (VI) with olefins [reaction (13)].[80,81] For the complexes $Cl_4M(CH_2)$, where M = Cr, Mo, or W, $\Delta G > 0$ and diminishes from 25 to 10 kcal mol^{-1} on passing from chromium to tungsten. The results of the calculations show that the free energy of formation of the metallacyclobutane intermediate can depend significantly not only on the nature of the metal but also on its ligand environment. For example, when two chlorine atoms are replaced by the oxo-ligand in the methylene complexes of Group VI metals, the formation of the metallacyclobutane is favoured by energy factors ($\Delta G \cong -20$ kcal mol^{-1}).[35]

The metallacyclobutane intermediate formed can decompose in different ways, which ultimately determines the direction of the entire reaction of the carbene complexes with olefins. The fact that the individual metallacyclobutane complexes of transition metals yield in the general case on photolytic decomposition the same compounds whose formation is to be expected in the reactions of the corresponding carbene complexes with olefins (Schemes 1 and 4) may serve as confirmation of this concept:

§ A possible mechanism of the activating influence of Lewis acids in such systems has been examined by J.Kress, M.Wesolek, J.P.Le Ny, and J.A.Osborn, Chem.Comm., 1981, 1039.

¶ According to Hoffmann's data,[89] the energy minimum corresponds to a four-centre structure with a distorted metallacyclobutane geometry, which is evidently a consequence of the approximation introduced by Rappé and Goddard.[90]

Scheme 4



(20)

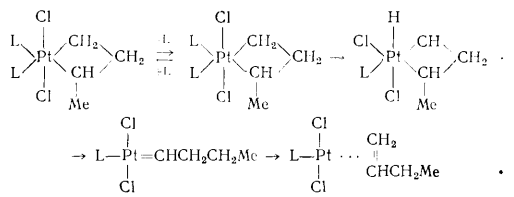
(21)

(22)

In this Section we shall attempt to analyse the factors promoting a particular pathway in the decomposition of metallacyclobutanes presented in Scheme 4.

In the metallacyclobutane intermediates arising in the reactions of nucleophilic carbene complexes of tantalum, niobium, or titanium with olefins, the formation of the products of the decomposition to the metal–olefin complex [reaction (20)] is regarded as a two-stage process involving β-elimination in the metallaring [reaction (14)]. The β-elimination reaction is characteristic to some extent of any mono- or di-alkyl compounds of transition metals[85,92,93] and experimental data confirm the possibility of its occurrence in metallacyclobutanes.[56,94–97]

The mechanism of reaction (20) has been studied in detail for individual metallacyclobutane complexes of platinum(IV).[97–101] It was found that, apart from the decomposition via β-elimination discussed above, this reaction can proceed via α-elimination in the metallacyclobutane with subsequent carbene–olefin isomerisation:[98,100,101]



where L = pyridine, 2-methylpyridine, or 2,6-dimethylpyridine.

Furthermore, the study of the distribution of the deuterium label in the decomposition products

$$(Py)_2Cl_2\overline{Pt[-trans\text{-}CH(Me)-CH(Me)-CD_2]}$$

and

$$(Py)_2Cl_2\overline{Pt-[-CH(Me)CMe_2CD_2]}$$

showed that the decomposition via α-elimination is the dominant process in such cases.[100] At the present time it is difficult to estimate the degree of general validity of the conclusion reached by Ling and Puddephatt,[100] but evidently the possibility of α-elimination must be taken into account in considering the rearrangements of metallacyclobutane intermediates.

The decomposition of the metallacyclobutane to the metal–carbene–olefin complex (21) leads to the formal reduction of the metal atom†, which imposes a limitation on the scope of the process: the metathesis decomposition of 18-electron compounds requires a preliminary change in the electron environment of the metal in the complex.

†The authors used Hoffmann's approach in which the alkylidene ligand is regarded as a neutral species.[34,89]

In the study of the mode of decomposition of 18-electron metallacyclobutane complexes of platinum having the general formula

$$L_2X_2\overline{Pt-CH_2-CH_2-CH_2}$$

(where X = Cl, or Br; L = TMED, bipy, or phen), it was established that the formation of ethylene is due to the possibility of the dissociation of the initial compound at the metal–halogen bond in a sufficiently polar solvent.[102] When the initial platinacyclobutane is a 16-electron complex of the type

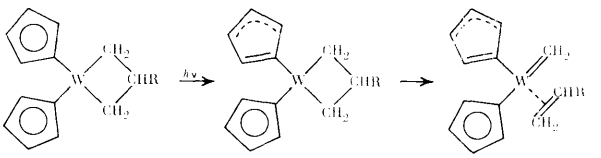
$$L_2\overline{Pt-CH_2-CH_2-CH_2}$$

[where L = PPh_3, $P(Alk)_3$, or bipy], its decomposition in this instance into ethylene and a methylene complex of platinum can be readily achieved in solvents of low polarity.[103]

It has been established that, regardless of the method of decomposition (thermolysis of photolysis), the main products of the reactions of 18-electron metallacyclobutane complexes of tungsten

$$Cp_2\overline{W-CH(R)CH(R)-CH_2}$$

are olefins obtained on decomposition to the metal–olefin complex (20). On the other hand, the decomposition to the metal–carbene–olefin complex takes place only on photolysis of the initial complexes, which is associated with the following chain of transformations via a 16-electron intermediate:[104,105]



(18$\bar{6}$) (16$\bar{6}$) (18$\bar{6}$)

The concerted decomposition of metallacyclobutanes with formation of cyclopropanes [Eqn.(22)] is a typical reductive elimination reaction.[106,107] Analysis of the change in the populations of the frontier orbitals in the decomposition of metallacyclobutanes, carried out by Hoffmann and co-workers, demonstrated the existence of an energy barrier, in terms of symmetry, for reactions (21) and (22): for the d^0–d^4 configurations of the metal in metallacyclobutane, decomposition to the metal–carbene–olefin complex takes place preferentially, while for the d^6 configuration the preferred reaction is reductive elimination with formation of cyclopropanes.[89] This conclusion is in good agreement with experimental data. In the decomposition of the metallacycles

$$Cp_2\overline{W-CH(R^1)CH(R^2)CH_2}$$

(R^1, R^2 = H or Me)[104,105] and

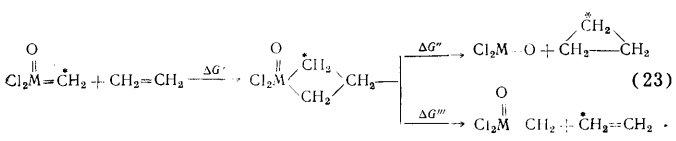
$$Cp_2\overline{Ti-CH_2-CHR-CH_2}$$

(R = iso-Pr or t-Bu),[80] there are virtually no cyclopropanes among the reaction products, while the metallacyclobutane complexes of quadrivalent platinum give rise fairly readily to a compound with a three-membered carbon ring on thermolysis and photolysis. It has been demonstrated[107] in relation to the deuterium-labelled complexes

$$Py_2Cl_2\overline{Pt-CH(R')CH(R^2)\cdot CH(R^2)}$$

(R = H, D, or Alk) that cyclopropanes are formed as a result of the concerted dissociation of the metal–carbon bonds, although the observed influence of solvent polarity on the rate and selectivity of reaction (22) indicate the possibility of a slight charge separation in the transition state.

The mode of decomposition of the metallacyclobutane intermediate depends not only on the characteristics of the electronic structure of the initial complexes examined above but can be determined to a large extent also by the stability of the final reaction products. The thermodynamic assessment of the preference for a particular decomposition pathway involves the determination of the free energies of all the components and it is wrong to the attempt the prediction of the equilibrium ratio of olefins and cyclopropanes on the basis of the free energies of these compounds,[108] as has been justifiably stated by Grubbs.[109] Indeed a non-empirical calculation of the potential surfaces for the cyclopropane formation and transalkylidenation reactions showed that the relative contributions of the two pathways are determined primarily by the transition metal and its ligand environment[35,91] (Table 3).



(23)

Table 3. Calculated free energies of formation and decomposition of the metallacyclobutane intermediates in the transalkylidenation and cyclopropane formation reactions[35] (kcal mol^{-1}).

M	$-\Delta G'$	$\Delta G''$	$\Delta G'''$
Cr	20	−2	20
Mo	24	42	24
W	18	43	18

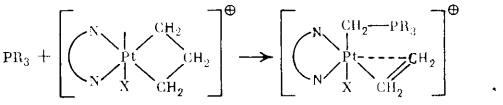
It follows from the data in Table 3 that, on passing from the chromium complex to the molybdenum and tungsten complexes, the metathesis pathway leading to the decomposition of the metallacyclobutane becomes energetically preferable to the decomposition with formation of cyclopropanes, which is associated with the increasing stability of the metal–carbon bond in the carbene complexes of molybdenum and tungsten.

The results of the calculations agree well with the experimental observation of the high strength of the binding of the carbene in the oxoalkylidene complexes of tungsten (XX) and (XXI),[110,111] which undergo the transalkylidenation reaction with olefins with a high degree of selectivity (Section (IV). The occurrence of the transalkylidenation reaction also when Mn^+CH_2 reacts with ethylene propene, and isobutene in the gas phase[113] has been explained by the presence of strong metal–carbon bonds ($E_b \approx 94$ kcal mol^{-1} [112,113]).

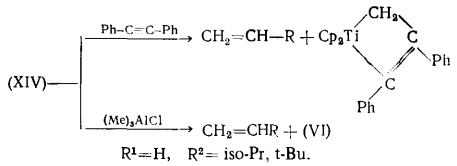
Thus, if there is competition between the two pathways (transalkylidenation and cyclopropane formation) for the carbene complex in the reaction with an olefin, then an increase of the strength of the metal–carbon bond leads to an increasing role of the former. An unusual experimental confirmation of the concept described is provided by data for the decomposition of metallacyclobutanes in the presence of compounds which stabilise the carbene complex in one way or another. For example, the yield of ethylene, the product of the metathesis decomposition of

$$L_2X_2\overline{Pt-CH_2-CH_2CH_2}$$

(L = TMED, Py, or bipy; X = Cl, Br, or I), increases sharply in the presence of trialkylphosphines,[102] which is apparently associated with the formation, in the course of the reaction, of ylide-like structures containing a stabilised methylene ligand (the possibility of such stabilisation has been demonstrated[114]):



It has been established[80] that, in the presence of tolane and dimethylaluminium chloride, the complex (XIV) undergoes highly selective metathesis decomposition:



Evidently in this case too the mode of decomposition is determined by the possibility of the formation of stable complexes containing a stabilised carbene ligand.

Examination of the reactions of individual carbene complexes of transition metals with unsaturated hydrocarbons shows that the change in the reaction pathway is caused in the first place by the electron distribution in the carbene ligand in the complex. Strongly electrophilic complexes such as $(CO)_5W(CHPh)$ or $[Cp(CO)_2Fe(CHR)]^+$ (R = H, Me, Ph) react with olefins exclusively with formation of cyclopropanes. The absence of coordination vacancies at the transition metal atom and the presence of the highly electrophilic $2p_z$ orbital in the carbene carbon in the complex gives rise to the similarity of the chemical reactivity of such complexes to those of free singlet carbenes.

Fischer complexes are electrophilic complexes in which the electrophilicity of the carbene ligand has been reduced as a result of the presence of electron-donating substituents in the α-position. The reactivity of such complexes depends significantly on the possibility of the formation of coordination vacancies at the transition metal. If the reaction conditions are such that coordination vacancies are not formed, then the Fischer complexes react with olefins like the complexes $(CO)_5W(CHPh)$ and $[Cp(CO)_2Fe(CHR)]^+$ examined above, although the relative reactivity of the Fischer complexes is much lower.

The possibility of the formation of coordination vacancies at the metal atom leads to the occurrence of a specific transalkylidenation reaction which is uncharacteristic of free carbenes and which reflects the capacity of the carbene complex to react with olefins via a metallacyclobutane intermediate. However, studies of the reaction of $(CO)_5W(CPh_2)$ with olefins have shown that in this case too the transalkylidenation is accompanied by the formation of a fairly large amount of cyclopropanes. Presumably the competition between the two decomposition pathways of the metallacyclobutane intermediate is caused by the impossibility of the formation in the electrophilic carbene complex of a strong metal–carbon bond, which is one of the main factors promoting the metathesis decomposition of the metallacyclobutane.

Nucleophilic carbene complexes react with olefins via the formation of metallacyclobutane intermediates. In the case of typical nucleophilic complexes such as $Cp_2Ta(CH_2)Me$ or $(PMe_3)_2Cl_3Ta(CHR)$ (R = Ph or CMe_3) the main pathway in the decomposition of metallacyclobutane intermediate is

β-elimination of a proton; as a result of reactions of such complexes with olefins, the carbene ligand is transferred to the olefin with formation of a set of new olefins.

When electron-donating ligands are introduced into the coordination spehre of the metal in nucleophilic complexes of tantalum and niobium, a decrease of the polarisation of the metal–carbon bond is to be expected. The relative role of β-elimination in the metallacyclobutane then diminishes and transalkylidenation becomes the main pathway in the reactions with such olefins. The oxoalkylidene complexes of tungsten (XX) and (XXI), which undergo a highly selective transalkylidenation reaction with olefins, also belong to nucleophilic complexes with a comparatively weak polarisation of the metal–carbon bond.

Thus, whereas the cyclopropane formation reaction and the reaction involving the transfer of the carbene ligand with formation of new olefins are characteristic of complexes with an appreciable polarisation of the metal–carbon bond, the transalkylidenation reaction is observed for complexes in which the metal–carbon bond is weakly polar.

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All-Union Lebedev Synthetic
Rubber Institute, Leningrad

Translated from *Uspekhi Khimii*, 53, 1172-1196 (1984) U.D.C. 541.6.12.03

Calculations of the Thermodynamic Properties of Polymers

L.I.Pavlinov, G.N.Marchenko, and Yu.A.Lebedev

The methods for the calculation of the thermodynamic parameters of various classes of polymers are examined. Together with a description of the classical phenomenological approaches, much attention has been devoted to the description of computational methods involving the modelling of the properties of polymers on the basis of the corresponding parameters of their low-molecular-weight analogues.
The bibliography includes 90 references.

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I. INTRODUCTION

The greatest amount of experimental thermodynamic data which have now accumulated in the chemistry of macromolecular compounds refer to a narrow range of linear vinyl polymers and a very small amount is concerned with polymers of other classes. At the same time a significant proportion of these data require a critical assessment and revision. This applies to a large extent to polymers with a complex structure of the repeating units (carbo-, and hetero-chain polyconjugated systems, cyclochain polymers, systems with a benzenoid structure of their macromolecules, etc.), for which it is frequently very difficult and sometimes impossible to estimate experimentally and accurately the contributions to the properties by various phase states of the chains and to take into account the presence of chemical defects and branches in the macromolecules as well as the influence of all possible impurities associated with the use of catalysts, initiators, etc. in the polymerisation process.

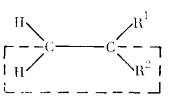
This is why modern theoretical methods for the calculation of thermodynamic properties have come to play an extremely important role in the determination of new thermodynamic characteristics of polymers and in the revision of values already available. The attempts at the employment for the solution of this problem of rigorous quantum-chemical methods, which are based on fundamental physical concepts, have encountered mathematical difficulties which cannot be overcome. This factor led to the creation of phenomenological methods, which in many instances make it possible to carry out the required calculations successfully and comparatively simply.

II. PHENOMENOLOGICAL METHODS

A large number of simple and complex phenomenological computational schemes have now been developed on the basis of many years of systematic studies of the thermodynamic properties of various groups of low-molecular-weight compounds.[1-16] Many of these schemes are used successfully in calculations of the thermodynamic parameters of saturated hydrocarbons, olefins, and the simplest organoelemental compounds. The parameters calculated are the heats of combustion and formation, heats of evaporation and fusion, heat capacities, entropies, etc. However, in relation to polymeric substances, the computational methods for the determination of the above characteristics have not yet been adequately developed. The virtual impossibility of the exact determination of the energies of non-valence and resonance interactions between the atoms in macromolecules and also of taking into account different phase states of the polymers may be indicated as the main cause holding back the application of modern computational schemes in such cases. Several more or less successful attempts at the extension to polymers of certain schemes which had been used earlier to calculate the properties of low-molecular-weight compounds are described below.

On the basis of the assumptions made in the calculation of the properties of polymers, the phenomenological methods can be divided by convention into two main groups. In schemes of the first group,[1-6] it is assumed that each given bond in any molecule or macromolecule has a constant characteristic energy. The overall energy of the molecule is found by the summation of the characteristic bond energies, applying corrections to the sum of the energies for the steric effects corresponding to the interaction of atoms not linked by valence bonds.

Calculations by means of these schemes of properties such as the enthalpies of atomisation and formation, which make it possible to obtain fairly accurate results (±0.1–0.2 kcal) for paraffinic and olefinic hydrocarbons, can be applied in principle to a polymer having the corresponding structure. The carefully developed Allen–Skinner scheme[2-4] has been used[11,16] for this purpose; this represents the structure of the polymer of the ethylene type $-CH_2-C(R^1R^2)-$ by a two-membered unstrained ring



in which the "characteristic" energies of the C–H and C–C bonds (including one C–C bond represented by a dashed line) were adopted in accordance with the data for methane and ethane taking into account corrections for the steric interaction of atoms not linked by valence forces. For example, the enthalpy of atomisation ΔH_a^0 (298) of a hydrocarbon polymer is given by the following expression in terms of this scheme:

$$\Delta H_a^\circ(298) = N_{CC}E_{CC} + N_{CH}E_{CH} + x\alpha_{CCC} - t\beta_{CCC} - s.1, \qquad (1)$$

where N_{CH} and N_{CC} are the numbers of C–H and C–C bonds in the elementary unit of the polymer, E_{CH} and E_{CC} are the C–H and C–C bond energies, α_{CCC} is the interaction energy for a pair of neighbouring atoms linked by valence bonds with the given carbon atom, x the number of such pairs, βCCC the trigonal energy of the interaction between three carbon atoms each of which is the nearest neighbour of the

other two, t the number of trigonal interactions, A the energy of the *gauche*-butane interaction, and s the number of such interactions.

Table 1 presents the results of the calculations in accordance with this scheme of the enthalpies of formation of a group of vinyl polymers and several new carbochain polymers corresponding to the hypothetical gaseous state of the polymer unit. In order to be able to compare the calculated ΔH^0_{form}(298, gas) and experimental heats of formation of the polymers in the condensed phase [ΔH^0_{form}(298, solid)] and also the calculated and experimental heats of polymerisation of the monomers corresponding to these quantities, the authors[11,16] made the not wholly correct assumption that the heat of evaporation (sublimation) of the elementary polymer units is equal to the heat of evaporation of the monomer. By the condensed state, the authors[11,16] understood any state of the solid polymer, ranging from wholly amorphous to partly crystalline.

On comparing the enthalpies of formation of polymers calculated in accordance with this scheme with the experimental quantities, the following conclusions may be drawn.

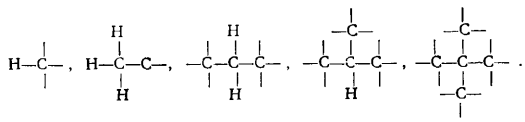
(a) For polyethylene and polymers which are monosubstituted derivatives of polyethylene, the agreement between the calculated enthalpies of formation of the polymers and the quantities found experimentally is entirely satisfactory.

(b) The scheme is altogether inapplicable to the calculation of the enthalpies of formation of 1,1-disubstituted derivatives of polyethylene [polyisobutylene, poly(vinylidene fluoride), poly-α-methylstyrene] and also for polymers characterised by considerable non-valence or resonance interactions (polymers with polar and bulky substituents, polymers with heteroatoms in the main chain, and polymers with conjugated bonds). The schemes of Tatevskii,[10] Laidler,[7] Cox,[8] and Benson[9] can be assigned to the second group of phenomenological schemes, which can be used in the calculation of the thermodynamic properties of polymers. A thermodynamic property ϕ is represented in these schemes by a linear function of the numbers of structural elements or bonds n_i in the repeating units of the polymer:

$$\varphi = \sum_i n_i f_i \ , \qquad (2)$$

where f_i is a characteristic constant referred to the structural element of the polymer unit or to a bond of type i.

These methods do not employ corrections taking into account the non-valence and resonance interactions of the atoms and are therefore simpler and more convenient than the methods in the first group, although they are less accurate. The number of characteristic parameters of the structural elements or bonds in these schemes is much larger, which permits calculations of properties taking into account the first-order sphere around the atoms in the structural element (Tatevskii's scheme[10]) or taking into account the hybrid state of the bonds between the carbon atoms (Laidler's and Cox's schemes[7,8]). For example, on the basis of the classification of the first method (Tatevskii's scheme), it is possible to obtain five types of structural elements and five types of coordination of the atoms (one for H atoms and four for C atoms) for alkanes taking into account the first sphere:



Both schemes indicated can be applied in principle to both carbochain polymers and polymers of other classes. The characteristic parameters of the bonds or groups of bonds are set up on the basis of a statistical treatment of a set of experimental data for different compounds in accordance with Eqn.(2).

Table 1 presents the results of calculations by Cox's method of the enthalpies of formation of a group of heterochain polymers and the corresponding enthalpies of polymerisation. In those cases where experimental data are available for the polymers considered, their comparison with the calculated values reveals considerable discrepancies (polyoxyethylene, polyformaldehyde, polytetrahydrofuran) probably as a consequence of the neglect in the calculations of the contribution of the non-valence interactions of the atoms.

Table 1. Comparison of the thermochemical characteristics of polymers calculated in accordance with the Allen–Skinner and Cox Schemes by Somayajla et al.[11] with the experimental values.

Polymer	$-\Delta H^0_{form}$(298), kJ unit^{-1}			$-\Delta H^0_{pol}$(298), kJ unit^{-1}		Refs.
	calc.		expt.	calc.	expt.	
	(gas)	(cond.)	(cond.)	(gas, gas)	(liq., cond.)	
Polyethylene	41.0	54.4	56.1	93.3	95.0	[53—55]
Polypropylene	67.8	86.2	83.7	88.3	85.8	[55, 56]
Polybut-1-ene	88.3	109.2	—	88.3	—	[45, 57]
Polyisobutene	102.5	123.0	88.7	85.8	51.5	[55]
Polybutadiene	—33.9	—13.0	—16.3	76.1	72.8	[58]
Polyisoprene	3.3	28.9	25.1	78.2	74.5	[59]
Polystyrene	—67.4	—22.6	—34.3	85.8	69.9	[60]
Poly-α-methylstyrene	—33.1	14.6	—35.1	84.9	35.1	[61]
Poly(vinyl chloride)	71.5	92.0	94.6	93.3	95.8	[61]
Poly(vinylidene chloride)	109.2	136.4	100.4	111.3	75.3	[61]
Poly(vinylidene fluoride)	415.5	432.6	474.0	84.9	125.5	[61]
Polytetrafluoro-ethylene	789.9	807.9	809.6	154.0	155.6	[4, 11, 63]
Polynitroethylene	37.2	74.9	83.6	82.0	90.8	[64]
Poly(acrylic acid)	396.6	442.7	—	63.2	77.4	[16, 72]
Polyacroleine	148.5	179.1	—	74.1	79.9	[16, 73]
Polyacrylonitrile	—90.0	—57.3	—	94.1	77.0	[16, 74]
Poly(ethyl vinylether)	225.5	—	—	85.4	—	[65]
Poly(vinyl acetate)	405.8	438.5	—	79.5	87.9	[16, 74]
Poly(methyl acrylate)	395.0	428.0	—	72.4	78.7	[66, 75]
Poly(methyl methacrylate)	428.9	464.8	433.5	87.9	56.5	[67, 76]
Poly(maleic anhydride)	508.8	552.7	—	96.2	58.6	[68, 77]
Polyformaldehyde	165.3*	190.0*	171.1	49.4	30.5	[55, 57]
Polyacetaldehyde	200.8*	227.6	—	44.4	—	[69]
Polyoxyethylene	167.4*	193.3*	—	114.6	94.6	[6, 69]
Polyoxystyrene	47.3*	101.7*	—	91.2	—	[66]
Polytetrahydrofuran	208.4*	240.6*	—	24.3	22.2	[69, 78]
Polycyclopropene	106.3	87.4	—	172.4	—	[70]
Polycyclopropane	65.7	86.6	84.1	118.4	115.9**	[71]
Polycyclohexane	131.4	164.4	168.2	8.4	—2.9**	[71]
Polycyclo-octane	164.0	208.8	224.3	39.7	34.7**	[71]
Polyacetylene	—58.6	—41.0	—	—	—	[57]
Polyacetonitrile	—68.6	—33.5	—	—	—	[57]
Polyacetone	244.8	276.6	—	—	—	[69]

*Calculation in accordance with Cox's scheme.
**Estimated theoretically.[16]

The best results were achieved in the calculation of the enthalpies and entropies of polymerisation of monomers with bonds of the type >C=C< and >C=C–C=C<.[12] Depending on the availability of initial experimental data, calculations have been carried out using Eqns.(3) or (4):

$$\left.\begin{aligned} \Delta H^0_{pol}\ (298) = \Delta H^0_c\ (298, \text{M}) - \Delta H^0_c\ (298, \text{P}) = \sum_i n_i^{\text{M}} f_{H,i}^{\text{M}} - \sum_i n_i^{\text{P}} f_{H,i}^{\text{P}}; \\ \Delta S^0_{pol}\ (298) = S^0(298, \text{P}) - S^0(298, \text{M}) = \sum_i n_i^{\text{P}} f_{S,i}^{\text{P}} - \sum_i n_i^{\text{M}} f_{S,i}^{\text{M}}\ ; \end{aligned}\right\} \qquad (3)$$

$$\Delta H^0_{pol}\ (298) = \sum n_{(i\to j)} f_{H(i\to j)},\quad \Delta S^0_{pol}\,(298) = \sum n_{(i\to j)} f_{S(i\to j)} \qquad (4)$$

In Eqn.(3) the quantities $\Delta H_c^0(298, M)$, $S^0(298, M)$, $\Delta H_c^0(298, P)$, and $S^0(298, P)$ are the enthalpies of combustion and the entropies of the monomer and the polymer unit respectively, $f_{H,i}^M$, $f_{S,i}^M$, $f_{H,i}^P$, and $f_{S,i}^P$ are constants for a structural element of type i in the monomer and polymer, and finally n_i^M and n_i^P are the numbers of structural elements of type i in the monomer and polymer. In Eqns.(4) the summation is carried out only over the corresponding pairs of interconvertible structural elements of type i in the monomer and of type j in the polymer and not over all types of structural elements, $f_{(i \to j)}$ being the corresponding constants.

The constants in Eqns.(3) and (4) were calculated from the experimental data for the following physical states (298.16 K, 101.325 kPa): for the gaseous (G) and liquid (L) states in the case of the enthalpy of combustion and only for the gaseous state in the case of the entropy.

Table 2 shows that comparison with the literature data of the enthalpies and entropies of polymerisation, calculated by Eqns.(3) and (4), of compounds such as alkenes, halogeno- and phenyl-alkenes, and styrene, acrylic acid, and methacrylic acid derivatives demonstrates an entirely satisfactory agreement between calculation and experiment. The discrepancies between the calculated and literature data are on average 6.3 kJ mol^{-1} for the enthalpies and 12.5 J mol^{-1} K^{-1} for the entropies.

The above comparison showed that the given scheme can be used to calculate the enthalpies and entropies of polymerisation via the $\rangle C{=}C\langle$ and $\rangle C{=}\overset{|}{C}{-}\underset{|}{C}{=}C\langle$ bonds in the corresponding monomers, for which the change in phase state during the reaction is of three types: monomer (G) → polymer (G), monomer (G) → polymer (S†), and monomer (L) → polymer (S). On the basis of Hess's law, the enthalpies and entropies of polymerisation of the monomers found can be easily converted into the enthalpies of formation and the entropies of the corresponding polymers (subject to the condition that the enthalpies of formation and entropies of the corresponding monomers are known). Unfortunately the method considered does not allow the determination of the given property of the polymer in the crystalline and amorphous-crystalline phases. At the same time the calculations of the thermochemical characteristics of the polymer in the condensed (amorphous) state and in the hypothetical gas phase calculated in this way can hardly ensure a reliable determination of a parameter as important as the energy of cohesion, because the constants employed in the calculation are averaged with respect to different classes of organic compounds and inaccurately reflect the energetic characteristics of specific types of compounds. Furthermore, the classification of different structural elements in the molecules on which the method is based makes it possible to take into account the interaction of atoms only in the immediate environment while long range interactions between atoms, due to the large dimensions of the macromolecules (the molecular weight factor), are completely disregarded.

Together with the difficulties enumerated above, one should also note that the given scheme in the version proposed by Grikina et al.[12] is subject to certain limitations. For example, it cannot be used to calculate the properties of heterochain, cyclochain, and heterocyclic polymers. Naturally, it is necessary to realise clearly that none of the available energy schemes is as yet able to predict correctly and take into account the individual characteristics of separate bonds in the macromolecule for many polymeric systems characterised by structural features such as the steric strain in the chain and bond conjugation.

Thus analysis of many empirical schemes for the calculation of thermodynamic properties of polymers employed nowadays shows in general that their scope is limited. When the structure of the elementary polymer units becomes more complex (for example, when cyclic, heterocyclic, and benzenoid structural elements appear in the polymer chain) the practical application of all the schemes considered becomes more difficult. At the same time, in connection with the vigorous progress in the theoretical and practical branches of polymer chemistry, the need to obtain new thermodynamic data and to test the values already available has arisen in the first place precisely for these complex polymer systems.

Table 2. Comparison with experimental data[16] of the enthalpies and entropies of the polymerisation of monomers via the $\rangle C{=}C\langle$ and $\rangle C{=}\overset{|}{C}{-}\underset{|}{C}{=}C\langle$ bonds calculated[12] by Tatevskii's method.

Monomer	Phase transition	$-\Delta H_{pol}^0(298)$, kJ mol^{-1}		$-\Delta S_{pol}^0(298)$, J mol^{-1}K^{-1}	
		calc.	Ref.16	calc.	Ref.16
$H_2C{=}C(CH_3)H$	G, G	85.8—87.4	88.3	159.4	166.9
»	G, S	101.3	104.2	—	—
»	L, S	83.3	85.8	113.8	116.3
$H_2C{-}C(C_2H_5)H$	G, G	87.1 : 84.5	88.3	156.5	166.5
»	G, S	103.3	—	—	—
»	L, S	84.1	83.7**	—	—
$H_2C{=}C(CH_3)_2$	G, G	78.2÷79.1	85.8	174.0	171.5
»	G, S	72.8	72.0	—	—
»	L, S	55.2	51.5	—	—
H_2C CH—CH CH_2*	G, G	71.5 (*cis*); 75.7 (*trans*)	76.1	133.9 (*cis*); 139.3 (*trans*)	—
»	L, S	65.3 (*cis*); 91.6 (*trans*)	72.8	—	85.8
$H_2C{=}$ CH—$C(CH_3)$ CH_2*	G, G	71.5	78.2	133.9	—
»	L, S	67.8	74.5	—	101.3
H_2C CHCl	L, S	103.3	95.8	—	—
H_2C CCl_2	L, S	73.2	75.3	—	—
$H_2C{=}C(C_6H_5)H$	L, S	69.0	69.9	106.7	104.6
$H_2C{=}C(CH_3)COOCH_3$	L, S	56.5	56.5	118.4	117.2
H_2CHC CHC_6H_5	L, S	36.8	35.1***	—	—
$H_2C{=}CHCOOH$	L, S	77.8	77.4	—	—
$H_2C{=}CHCOOCH_3$	L, S	77.8	78.7	—	—
$H_2C{=}C(OCOCH_3)H$	L, S	86.6	87.9	—	—
$H_2C{=}C(CH_3)COOC_6H_{11}$	L, S	56.5	51.0	—	—
$H_2C{=}C(CH_3)COOC_6H_5$	L, S	56.5	51.5	—	—

*A double bond in the centre of the monomer unit is formed in the polymer.

**Data of Furukawa and Reilly.[50]

***Data of Dainton and Ivin.[6]

Note. G = gas, L = liquid, S = solid (Ed.of Transaltion).

In order to overcome the difficulties indicated, attempts have been made in the last decade to develop procedures for calculations on the thermodynamics of polymers based on the principle of similarity.[15,18,19] According to this principle, the study of the properties of complex polymers is replaced by the study of the properties of a series of model compounds which reproduce the structure of integral repeating polymer units. Here there is no need to employ a large number of increments other than those necessary to take into account the influence of the two end groups of the model compound on the properties of the repeating units. The practical application of this modelling principle

† S = solid (Ed.of Translation).

provides for the employment of experimental data characterising the given low-molecular-weight model or system of models. On the other hand, the experimental procedures for the determination of thermodynamic data for model substances (combustion, calorimetry, reaction calorimetry, measurements of heat capacity, etc.) are themselves usually less laborious and at the same time more accurate than in the direct investigation of the properties of the polymers themselves.

Different versions of the above modelling method, including the mathematical form of modelling,[40] in which the properties of complex polymers are obtained from those of less complex polymers (the interpolation method) are examined below.

III. MODELLING METHODS

1. The Method of Linear Correlations of the Parameters of Model–Polymer Systems

The methods of similarity theory,[13,14] widely and successfully employed in the chemistry of individual low-molecular-weight compounds, have not as yet been developed adequately in polymer chemistry. A study in which the applicability of the rules of similarity theory to polymers has been demonstrated can be regarded as one of the first steps in this direction.[15]

A modelling method, the essential feature of which consisted in the selection and investigation of the thermodynamic parameters of individual compounds modelling the structure of sections of the macromolecular chains whose length was not less than that of the single repeating elementary unit, has been employed in the determination of the thermodynamic parameters of polymers.[15] Thermodynamic data corresponding to specific sequences of models and polymers investigated previously served as the basis for the calculation of the uninvestigated analogous properties of other polymers. This type of calculation can be performed using a statistical approach[15] in which the correlation coefficient r is used to investigate the interrelation of the properties indicated.

On the basis of general mathematical considerations,[14,20] there should be a linear relation between two functions $f(x, y_1, z_1, \ldots)$ and $f(x, y_0, z_0, \ldots)$, where $y_1, z_1, \ldots$ and $y_0, z_0, \ldots$ are any two sets of fixed values of the arguments y and z, while x is a variable. Here $f(x, y_1, z_1, \ldots)$ cannot be linear with respect to the argument x itself.

The application of this approach to the thermodynamic parameters of any one polymer [$\Delta H_c^0(298)$, $\Delta H_{form}^0(298)$, $S^0(298)$, $\Delta G_{form}^0(298)$, etc.] leads to the expression

$$\varphi_P(x_1, x_2, x_3, \ldots, x_i, \ldots) = \varphi_P^0(x_1^0, x_2^0, x_3^0, \ldots, x_i^0, \ldots) + \sum_i x_i' + \alpha \sum_i \sum_j x_i' x_j' + \alpha^2 \sum_i \sum_j \sum_k x_i' x_j' x_k' + \cdots \quad (5)$$

where x_i', x_j', ... are structural parameters which depend respectively on the arguments x_i, x_j, ...; x_1^0 and x_2^0 are any standard values of the arguments, α is a constant, and $i \neq j \neq k$.

If all the quantities of type x_i' are constant except for x_j', which we shall assume arbitrarily to depend on the nature of the substituent or a group of substituents in the repeating polymer unit, then we obtain the expression

$$\varphi_{P,j} = \varphi_{P,0} + b_P x_j' \quad (6)$$

where $\phi_{P,j}$ and b_P are constants related to parameters of type x_i' corresponding to structural elements whose effect on $\phi_{P,j}$ in a similar series of polymers remains unchanged. The subscript "P" denotes the first combination of constant factors corresponding to the polymer.

On passing to model compounds, it is possible to consider the change in the same quantity x_j' for certain fixed values of the remaining quantities x_i':

$$\varphi_{M,j} = \varphi_{M,0} + b_M x_j' . \quad (7)$$

The subscript "M" denotes the second combination of constant factors corresponding to the model.

From Eqns.(6) and (7), we obtain the expression

$$\varphi_{P,j} = \Delta\varphi_0 + \beta\varphi_{M,j} \quad (8)$$

where $\Delta\phi_0 = \phi_{P,0} - \phi_{M,0}(b_P/b_M)$ and $\beta = b_P/b_M$; it follows from Eqn.(8) that the quantities $\phi_{P,j}$ and $\phi_{M,j}$ depend linearly on one anther, i.e. there is a correlation between them.

It is noteworthy that this conclusion applies to homogeneous interactions in which the chain in the structure of the substituents in the polymer and in the model leads to an additive change in the properties of the system.

Table 3. Parameters of the linear correlation (8) in the studies of Korshak and co-workers[15] and Marchenko[18] describing the relation between the thermodynamic properties of a series of polymers and model compounds.

Characteristic	Phase	N	$\Delta\varphi$	β	r	α, %
		Correlation pairs of type (I)				
$\Delta H_{form}^0(298)$, kJ mol^{-1}	(G)-(G)	12	51.664	1.0434	0.9989	0.1
	(L)-(L)	10	48.723	1.0120	0.9997	0.1
	(Cr)-(Cr)	5	55.011	1.0540	0.9947	0.1
	(Φ_j)-(Φ_j)	20	48.149	1.0050	0.9980	0.1
$S^0(298)$, J mol^{-1}K^{-1}	(G)-(G)	5	−175.846	1.0225	0.9974	0.1
	(L)-(L)	5	−136.511	1.0757	0.9972	0.1
	(L)-(G)	5	−213.903	1.0124	0.9857	1.0
	(Cr)-(Cr)	9	−87.153	0.8150	0.9946	0.1
$C_p^0(298)$, J mol^{-1}K^{-1}	(G)-(G)	4	14.263	0.7772	0.9982	1.0
		Correlation pairs of type (II)				
$\Delta H_{form}^0(298)$, kJ mol^{-1}	(G)-(G)	5	52.413	1.0012	0.9980	0.1
	(G)-(L)	4	68.379	0.9262	0.9981	1.0
	(L)-(L)	4	54.241	0.9791	0.9995	0.1
$S^0(298)$, J mol^{-1}K^{-1}	(G)-(G)	4	−177.749	1.0294	0.9982	1.0
	(L)-(L)	5	−135.850	1.0702	0.9950	0.1
	(L)-(G)	4	−273.249	1.1546	0.9869	1.0
$C_p^0(298)$, J mol^{-1}K^{-1}	(G)-(G)	4	14.263	0.7772	0.9982	1.0

Remarks. The correlation of the properties for the physical states designated by (Φ_j) – (Φ_j) combines the variations of the properties in the pairs, in identical states, into a single linear variation; notation: N is the number of pairs, $\Delta\phi$ and β are parameters of Eqn.(8), r is the coefficient of the linear correlation of the properties, and α is the probable error of the correlation.
Note. G = gas, L = liquid, Cr = crystalline (Ed.of Translation).

According to the procedure proposed by Korshak and co-workers,[15] the choice of the polymers and the corresponding models in setting up a correlation series of properties ($\phi_{P,j}$ and $\phi_{M,j}$) must be made assuming an identical hypothetical process (conventional transition) for all the pairs,

relating, in conformity with Eqn.(8), the properties of the polymer unit $(-[-P-]_n-)$, the model $(R^1P_mR^2)$, and the compound R^1R^2:

$$R^1P_mR^2 \rightarrow \frac{m}{n}(-[-P-]_n-)+R^1R^2\ ; \quad m = 1, 2, \ldots, 4;\ n \rightarrow \infty\ . \tag{9}$$

According to this scheme, the polymer macromolecule can be obtained from the molecules of the model compound as a result of the abstraction of the elementary substituents and the formation of the molecules R^1R^2 from them. Compounds whose molecules undergo minimal chemical changes in reaction (9) can be usefully selected as models; in this sense R^1R^2 can be H_2, H_2O, HCl, etc. For example, the properties of vinyl polymers have been calculated[15,18] (Table 3) in conformity with conventional transitions of the type $HP_mH \rightarrow m-[-P-]- + H_2$ ($m = 1, 2$), which permitted the use of correlation pairs of two types:

	Pair (I)	Pair (II)
Polymer (P)	$-CH_2-CHR-$	$-C(R^1R^2)-C(R^3R^4)-$
Model compound (M)	$H-[-CH_2-CHR-]_m-H$ ($m = 1, 2$)	$H-[-C(R^1R^2)-C(R^3R^4)-]_m-H$ ($m = 1$)

In order that calculations based on Eqn.(8) should yield the properties $\phi_{P,j}$ uncomplicated by the influence of the polymer end groups and hence referring to formation of the elementary polymer unit, it is necessary that the degree of polymerisation of the polymers involved in the correlation series should be fairly high. In those cases where it is difficult to select a model compound for the polymeric substance (for example, for a copolymer) corresponding to Scheme 9, it is possible to use a conventional transition with two model compounds R^1PR^2 and R^1SR^2, whose thermodynamic characteristics are known, i.e. a transition of the type

$$R^1PR^2 + R^1SR^2 \rightarrow \frac{1}{n}(-[-PS-]_n-) + 2R^1R^2, \tag{10}$$

where P and S correspond to the monomeric units of the copolymer.

2. Estimation of the Reliability of the Linear Correlation of the Parameters of the Model–Polymer Systems

We shall now consider the question of the reliability of the linear correlation method in relation to the correlation series of parameters for model–polymer systems in which the polymers belong to the vinyl series (Table 3). The constants of the correlation Eqn.(8), needed for the calculation of the thermodynamic parameters of the polymers, were found for three phase states of the latter: ideal gaseous, condensed (amorphous), and ideal crystalline. The coordinates of the reference points for their determination were the tabulated thermodynamic properties of model compounds[17] and certain reliable characteristics of the polymer systems obtained both experimentally (for the amorphous and amorphous-crystalline states of the systems—data from Ref.16#) and by calculation (for the ideal gaseous and crystalline states—data by Korshak and co-workers[15] and Marchenko[18] obtained by extrapolating the properties of oligomers to infinite molecular weight).

Statistical analysis of the correlation between the thermodynamic parameters of the vinyl polymers and models (Table 3) carried out using the Student t-statistic[15,18] showed that it is quite possible to describe this correlation by a linear regression equation with a probable error of the order of 0.1–1.0%. Furthermore, this analysis showed that the probable error can be reduced to $\alpha \leq 0.1\%$ (fiducial probability $P \geq 0.999$) in those cases where the most accurate thermodynamic parameters of the polymers and models are used as the coordinates of the reference points of the regression equation.

It should also be noted that, when there is a correspondence between the phase states of the vinyl polymers and model compounds, the correlation between their enthalpies of formation and entropies can be described on the basis of the constant difference principle, in conformity with which one puts $\beta = 1$ in Eqn.(8) with a probable error of 0.1–1.0%. The application of this method to calculations of the thermodynamic parameters of a series of polymers of practical importance has also been examined by Korshak and co-workers.[19]

The discrepancies between the results of the calculation in accordance with this scheme of the enthalpies of formation, entropies, and heat capacities of polymers and the experimental data, which exceed the probable error of the correlation by 1–5%, can arise, in particular, because the experimental data refer to polymer specimens which have been inadequately investigated from the standpoint of their physical state. More notable discrepancies can be a consequence of inaccuracies in the study of the chemical structures of the polymer specimens.

3. Methods for the Extrapolation of the Properties of Polymer-Analogue Model Compounds to Infinite Molecular Weight

We shall consider yet another version of the modelling method whereby it is possible to calculate effectively the standard thermodynamic parameters of polymers and which will be referred to as the method of extrapolation of the properties of polymer-homologues to infinite molecular weight.[18,19] Hitherto undeservedly little attention has been devoted to studies concerning the calculation of the thermodynamic parameters of polymeric substances. During the last 30 years, only about ten investigations have been reported[21–32] in which mainly the physical characteristics of amorphous polymers were estimated on the basis of the properties of n-paraffins and certain other simplest homologous series (in particular, the densities, surface tensions, cohesion energies, dielectric constants, etc. have been determined) and only a few communications[28–30] have been devoted to the estimation of the thermodynamic parameters of liquid and gaseous paraffinic hydrocarbons with infinitely long chains both unbranched and branched [branches of the type of $-CH(CH_3)-$ and $-C(CH_3)_2-$ at each third, fourth, and fifth carbon atom in the chain]. For example, the heat of formation (per $-CH_2-$ group) of an infinite polymethylene chain in the gaseous state has been found by this method[28] as −20.61 kJ mol^{-1}. The entropy increment per $-CH_2-$ group has been calculated for the same polymer by an analogous procedure[29] as 38.95 J mol^{-1} K^{-1}.

The method of calculation of the thermodynamic properties of polymers considered here is based on the concept of polymeric substances as the limiting members of the corresponding polymer-analogue series of substances; the possibility of estimating these properties by extrapolating the specific characteristics of the members of the polymer-analogue series to infinite molecular weight follows directly from this concept. The application of the method indicated requires the knowledge of the characteristic features of the changes in the thermodynamic properties in the polymer-analogue series of substances, starting with the lowest members of the series, normally employed as models of polymers, and ending with the highest limiting members of the series, whose mixture constitutes in effect real polydisperse polymers. If one begins with the hypothesis that

There is no reference 16 in the Russian text (Ed.of Translation).

the contributions to the parameters of the repeating structural units and the end groups are additive for the highest members of the series, while only small deviations from additivity are characteristic of the lowest members, then a thermodynamic property of the molecule Φ_n, corresponding to the nth member of the series with a molecular weight M_n, can be represented in the following form:

$$\Phi_n = \sum_{i=1}^{n+2} m_i\varphi_i + \delta_n = m_1\varphi_1 + m_2\varphi_2 + nm_0\varphi_0 + \delta_n , \quad (11)$$

where ϕ_0 denotes the specific contribution to the property Φ_n of the repeating structural element of a chain with a mass m_0, ϕ_1 and ϕ_2 are the specific contributions to the property Φ_n by the two end groups with masses m_1 and m_2 respectively, and δ_n is a small correction which becomes a maximum for $n = 0$ (this value characterises the end groups of molecules of the given series) and becomes zero for the highest members of this series, i.e. $\lim_{n\to\infty} \delta_n = 0$.

The nature of the correction δ_n is such that it defines the change in the intensity of the non-valence intramolecular and intermolecular interactions of the atoms and the deformations of the valence angles in the sequence of molecules constituting the given polymer-analogue series. It is quite understandable that it must be taken into account in determining the exact dependence of the thermodynamic properties of the members of the series on the molecular weight. In a study of the variation of the enthalpies of formation of the lowest members of the homologous series of hydrocarbons in the gaseous state, Prosen et al.[32] established that δ_n can be neglected not at $n = \infty$ but much earlier when the number of repeating CH_2 groups in the hydrocarbon corresponds to $n \geq 4$. Thus, starting with $n_0 = 4$, the quantity δ_n becomes zero regardless of the nature of the end groups of the hydrocarbons. For other, longer repeating structural units, for example such as $-C_6H_4-$, $-C_6H_4O-$, $-C_6H_4NHCO-$, etc., we have $n_0 < 4$.

Thus if members corresponding to $n < n_0$ are removed from the homologous series of compounds, then the properties of the remaining members can be described with the aid of only the linear part of Eqn.(11).

In order to characterise the properties of members of a polymer-analogue series, it is useful to introduce two constants which are independent of the molecular weight of the members of the given series:

$$k_\varphi = (m_1\varphi_1 + m_2\varphi_2)/m_0\varphi_0; \quad k_m = (m_1 + m_2)/m_0 . \quad (12)$$

On the basis of Eqns.(11) and (12), it is possible to calculate the required specific contributions to the property Φ_n of the repeating structural element of the polymer in the following manner:

$$\varphi_0 = (\Phi_n - \delta_n)/(k_\varphi + n)m_0 . \quad (13)$$

It is noteworthy that the magnitude of this contribution should not in principle depend on the form of the end groups of the molecules of the polymer-analogue series, which are in the gaseous state or in a condensed phase. On the other hand, the specific value of the given property ϕ_n determined directly from the experimental results contains in all cases a contribution by the end groups of the molecule of the nth member of the series, which depends on n, since the expression

$$\varphi_n = \Phi_n/M_n = \Phi_n/(k_m + n)m_0 , \quad (14)$$

corresponds to it. It follows from a comparison of Eqns.(13) and (14) that

$$\varphi_n = \varphi_0[1 + (k_\varphi - k_m)/(k_m + n)] + \delta_n/M_n \quad (15)$$

where δ_n/M_n corresponds to the specific deviation of the property from additivity.

If one confines oneself in the treatment of a polymer-analogue series only to its terms ($n \geq n_0$) for which one can neglect the ratio δ_n/M_n, then Eqn.(15) assumes a form convenient for the calculation of ϕ_0:

$$\varphi_n = \varphi_0[1 + (k_\varphi - k_m)/(k_m + n)] . \quad (16)$$

As can be seen from Eqns.(15) and (16), by extrapolating ϕ_n to $1/(k_m + n) = 0$, it is easy to obtain the increment of the thermodynamic parameter of the polymer ϕ_0. Furthermore, on the basis of Eqn.(16), it is convenient to estimate the limiting molecular weight of the chains, at and above which the difference between ϕ_n and ϕ_0 should be neglected. Since Eqn.(16) is a fractional-linear function of n, for which $\phi_n/\phi_0 = 1$ is one of the asymptotic forms, the specific property ϕ_n obtained directly from the experimental results can be assumed equal to ϕ_0 only for fairly large values of $n \to \infty$.

When determining the constant parameters k_ϕ and ϕ_0, one can employ, together with Eqns.(15) and (16), simple relations which use the known values of the properties of only two members of the series, for example Φ_n for the nth member and Φ_r for the rth member ($n > r$):

$$k_\varphi = (n\Phi_r - r\Phi_n)/(\Phi_n - \Phi_r); \quad \varphi_0 = (\Phi_n - \Phi_r)/(n - r)m_0 . \quad (17)$$

As stated above, the choice of the given members of the series is limited to the group of substances for which r is greater than a limiting values n_0, starting from which the change of the properties in the series involves a regular increment in $\phi_0(\delta_{n_0} = 0)$.

Since the choice of members of the polymer-analogue series with $n \geq n_0$ for different chain lengths has a negligble influence on the parameters k_ϕ and ϕ_0 found from Eqn.(16), it is logical to suppose that their values do not change also in the case of a polydisperse mixture made up of molecules of the same series. In this case it is clear that the ratio of the properties $\bar{\phi}_n$ and ϕ_0 in the nth fraction of the polydisperse polymer, characterised by the number-average quantities $\bar{\Phi}_n$ and degree of polymerisation $\bar{n}$, can be obtained with the aid of an expression analogous to Eqn.(16):

$$\bar{\varphi}_n/\varphi_0 = 1 + (k_\varphi - k_m)/(k_m + \bar{n}) , \quad (18)$$

where $\bar{\Phi}_n = \phi_0$ only when $\bar{n} \to \infty$. When $\bar{n} = 10^3$ and $k_\phi - k_m = 1$, the approximation $\bar{\phi}_n = \phi_0$ leads to an error of 0.1% in the determination of ϕ_0 and of 10% in the molar quantity for $m_0 = 100$.

It is noteworthy that the character of the variation of the thermodynamic properties of polymeric substances as a function of $\bar{n}$, expressed by Eqn.(18), is general. In particular, it can be shown that the polymerisation equilibrium constants corresponding to the stages involving the interaction of the monomer with the initiator (K_1) and its dimerisation (K_2), trimerisation (K_3), etc. obey analogous relations. The variation of the equilibrium constants in the sequence K_1, K_2, ..., K_n characterises primarily the variation of the thermodynamic properties of compounds in a polymer-analogue series corresponding to this sequence. In the polymerisation of a monomer M in the presence of an initiator XY

$$XY + M \overset{K_1}{\rightleftarrows} XMY,\ XMY + M \overset{K_2}{\rightleftarrows} XM_2Y, \ldots,\ XM_{n-1}Y + M \overset{K_n}{\rightleftarrows} XM_nY$$

which is frequently encountered in practice, the Tobolsky approximation[33] $K_1 \neq K_2$, $K_2 = K_3 = \ldots = K_n = \ldots = K$ holds with adequate accuracy. From it, it is easy to obtain an equation relating the equilibrium constant K to the number-average degree of polymerisation of the polymer chains:

$$K = \frac{1}{[M]}\left[1 - 1/(\bar{n} - 1)\right] , \quad (19)$$

where [M] is the equilibrium concentration of the monomer. Subject to the condition that $\bar{n} \to \infty$, we have $K_\infty = 1/[M]$ and consequently

$$K = K_\infty [1 - 1/(\bar{n} - 1)] . \quad (20)$$

It can be seen that the character of relations (18) and (20) is the same although, compared with Eqn.(20), the initial significance of the constants k_ϕ and k_m, inherent in Eqn.(18), is clearly different. In this case Eqn.(20) shows that, when the Tobolsky approximation is valid, the true value of the equilibrium constant of the n-merisation stage is smaller than the limiting equilibrium constant K_∞ (corresponding to the formation of infinitely long chains) by an amount inversely proportional to the number-average degree of polymerisation of the product.

Another example, confirming the general character of the variation of the thermodynamic properties in a polymer-analogue series, expressed by Eqn.(18), is the analogous dependence of the enthalpy of polymerisation of the monomer on the number-average degree of polymerisation. For example, in the case of α-methylstyrene, this relation has the following form: [34]

$$\Delta H^0_{pol}(298)\ (\text{kJ mol}^{-1}) = 34.74\ (1 + 2.205/\bar{n}). \quad (21)$$

It is possible to quote a much greater number of similar examples. However, here it is more important to note that in all such cases, where the limiting parameter ϕ_0 is found by extrapolating function (18) to the limit $1/(k_m + \bar{n}) = 0$, it is necessary to make preliminary experimental determinations of the number-average values of the property $\bar{\phi}_n$ and degree of polymerisation $\bar{n}$ for several fractions of the polymer. These are extremely laborious and at the same time need to be fairly accurate.

Thus, in order to obtain fundamental thermodynamic characteristics of the polymers such as ϕ_0, which are independent of the average molecular weight and the molecular weight distribution of the polymer macromolecules, one can employ, on the one hand, the version of the modelling method examined above and the corresponding Eqns.(15) and (16) and, on the other hand, one can carry out a direct experimental study of the properties of different fractions of the polymer itself and then calculate ϕ_0 from Eqn.(18). Although the second procedure is now more commonly used in practice, the results obtained by this method as a rule require confirmation and refinement, since for most of them it is impossible to find corrections for the different phase states of the polymer and to allow for the presence of chemical cross-links and chain branches as well as contaminations associated with the employment of initiators, catalysts, emulsifying agents, etc. in the polymerisation process. On the other hand, extrapolation of the properties of the individual models of compounds to $n \to \infty$ in accordance with Eqn.(16), which is used in the first procedure, does not require a complex allowance for corrections associated with the specific features of the synthesis of the polymer and, what is particularly important, this method makes it possible to determine with satisfactory accuracy the properties of polymer chains in three ideal states of aggregation: in the solid (crystalline), liquid, and ideal gas states (Table 4). With the aid of extrapolation, it is then possible to proceed from ideal characteristics to the thermodynamic properties of a real amorphous-crystalline polymer, in the case where the degree of crystallinity of the polymer is known. For example, the enthalpy of formation of a 100% crystalline polymer can be extrapolated to the real degree of crystallinity w on the assumption that the difference between the enthalpies of formation of the polymer for degrees of crystallinity of 0% and w% is proportional to the degree of crystallinity:

$$\Delta H^0_{form}(298;\ w) = \Delta H^0_{form}(298;0\%) - w\ [\Delta H^0_{form}(298;0\%) - \Delta H^0_{form}(298;100\%)].$$

Finally, it is quite possible to infer the energy of formation of the real crystal lattice of the polymer from the difference between the enthalpies of formation of the polymer in the ideal gaseous and crystalline states. [30]

Table 4. Dependence of the specific thermodynamic properties of compounds in homologous series on the molecular weight. [18]

Compound	n	State	φ_0	$(k_\varphi - k_m)\varphi_0$	r
			$\varphi = \Delta H^0_{form}$ (298), kJ g^{-1}		
$H(CH_2)_{2n}H$	2—12	G	−1.469	−1.452	−0.9972
»	2—10	L	−1.827	−1.477	−0.9981
»	5—12	Cr	−2.404	−1.114	−0.9932
$H(CH_2)_{2n+1}H$	2—8	G	−1.472	−1.395	−0.9982
»	2—8	L	−1.815	−1.532	−0.9980
»	5—12	Cr	−2.093	−0.720	−0.9937
$H(CH_2)_nH$	2—20	G	−1.469	−2.906	−0.9991
»	4—20	L	−1.825	−2.962	−0.9988
»	10—24	Cr	−2.100	−1.869	−0.9600
			$\varphi = S^0$ (298), J g^{-1}K^{-1}		
$H(CH_2)_{2n}H$	2—40	G	2.782	5.299	0.9998
»	2—40	L	2.290	3.794	0.9625
»	10—16	Cr	1.737	2.361	0.9783
$H(CH_2)_{2n+1}H$	2—9	G	2.789	5.275	0.9998
»	2—9	L	2.300	3.524	0.9994
$H(CH_2)_nH$	4—20	G	2.782	10.599	0.9960
»	4—20	L	2.319	6.843	0.9988
			$\varphi = C^0_p$ (298), J g^{-1}K^{-1}		
$CN(CH_2)_{2n}H$	1—6	G	2.776	4.631	0.9999
$H(CH_2)_{2n}H$	1—10	G	1.623	1.292	0.9732
$H(CH_2)_nH$	1—19	G	1.630	1.900	0.9950
$CN(CH_2)_{2n}H$	1—6	G	1.640	−0.643	−0.9995
$CN(CH_2)_{2n+1}H$	1—5	G	1.620	−0.565	−0.9993

Remarks. ϕ_0 and $(k_\phi - k_m)\phi_0$ are parameters of correlation (16), r is the coefficient of the linear correlation, and α is the error of the correlation, equal in all cases to 0.1%.
Note. G = gas, L = liquid, Cr = crystalline (Ed.of Translation).

A useful consequence of Eqn.(16) is the possibility of employing the relation between two different properties ψ_n and ϕ_n of compounds of the same polymer-analogue series (for compounds of two different series characterised by the same values of k_m and n) in the form

$$\psi_n = A + B\varphi_n , \quad (22)$$

where $A = \psi_0(k_\phi - k_\psi)/(k_m - k_\phi)$ and $B = \psi_0(k_\psi - k_m)/\phi_0(k_\phi - k_m)$. The constants used to determine A and B have the same significance as in Eqn.(16).

Thus relations similar to Eqn.(22) can also be used to extend the range of data both on the compounds of polymer-analogue series and the polymers themselves.

4. The Reliability of the Extrapolation Method

In order to estimate the reliability of the calculations by the method involving the extrapolation of the thermodynamic parameters of polymers in the ideal gaseous and condensed states, Eqn.(16) has been applied [18] to thoroughly investigated homologous series of compounds of the type $R^1(CH_2)_nR^2$

(R^1, R^2 = H, H, or CN, H).[17] For this purpose, the thermodynamic parameters of compounds of the corresponding series [$\Delta H^0_{form}(298)$, $S^0(298)$, and $C^0_p(298)$] were treated as functions of $1/(k_m + n)$ alternately for three ideal physical states—gaseous, liquid, and crystalline. Table 4 shows that the above relations can be fitted by linear functions of $1/(k_m + n)$ of the type of Eqn.(16) with a high degree of reliability. This is indicated, in particular, by the closeness of the coefficients of linear correlation obtained to unity. Furthermore, statistical analysis of the relations using the Student t-statistic showed that a linear correlation of type (16) holds with a fiducial probability $P \geq 0.999$ for the given homologous series (the error of the correlation $\alpha \leq 0.1\%$).

Extrapolation of the specific values of the thermodynamic functions of n-paraffins to $1/(k_m + n) = 0$ yields the enthalpies of formation and entropies of polyethylene corresponding to three phase states of its macromolecules: ideal gaseous, liquid, and crystalline. Table 4 shows that the results of this extrapolation in the series of even and odd n-paraffins differ somewhat. The difference, for example for the increment of the enthalpy of formation per $-CH_2-$ group in the crystalline state is 0.6%, which exceeds severalfold the experimental error of the given characteristic for n-paraffins (~0.1%). The appearance of this effect may be attributed to different symmetries of the even and odd molecules. The studies by Muller and Lonsdale,[35] Schaerer et al.[36], and Piper[37] showed that the alternation of the melting points between the even and odd n-paraffins (the melting point is higher for the even members) is due to the alternation of two different types of their crystal structure: the orthorhombic modification of the short odd members of the series alternates with the triclinic modification of the even members having $n_C \leq 28$. On the basis of the results of these studies, one can assume that the extrapolation of the thermodynamic properties of crystalline n-paraffins with an even number of carbon atoms ($4 \leq 2n_C \leq 28$, Table 4) to the region of infinite molecular weights yields the properties of the triclinic crystalline modification of polyethylene. An analogous operation for n-paraffins with an odd number of carbon atoms makes it possible to estimate the thermodynamic characteristics of the orthorhombic crystalline modification of polyethylene, which is the commonest type of the unit cell for this polymer.[38]

The results obtained by Marchenko[18] agree with other data.[16,28,29] In particular, the increments in the enthalpy of formation and entropy per $-CH_2-$ group for the gaseous state of the chains of this polymer, listed in Table 4 [$\Delta H^0_{form}(298, \text{gas}) = -1.469 \times 14.027 = -20.602$ kJ mol^{-1} and $S^0(298, \text{gas}) = 2.782 \times 14.027 = 39.02$ J mol^{-1} K^{-1}] are consistent with the enthalpy of -20.61 kJ mol^{-1} and the entropy of 38.93 J mol^{-1} K^{-1} from other studies.[28,29] Furthermore, linear interpolation of the increments of the enthalpy of formation of the fully crystalline state [$\Delta H^0_{form}(298, \text{cryst.}) = -2.093 \times 14.027 = -29.36$ kJ mol^{-1}] and the fully amorphous state [$\Delta H^0_{form}(298, \text{amorph.}) = -1.815 \times 14.027 = -25.46$ kJ mol^{-1}] yields the enthalpy of formation (-28.19 kJ mol^{-1}) for the real amorphous-crystalline state of polyethylene with a degree of crystallinity of ~70%,[39] which agrees well with the experimental value (-28.03 kJ mol^{-1}).[16]

5. The Difference Interpolation Method

The possibility of applying the relations of difference interpolation to calculations of the physicochemical properties of polymers has been pointed out in a number of studies.[18,19,40] According to the difference interpolation method, a thermodynamic property ϕ, which depends on different sets of structural elements m_1, m_2, ..., m_n, can be represented in the form

$$\varphi(m_1, m_2, \ldots, m_n) = \varphi(0, 0, \ldots, 0) + \sum_k C^{\lambda_{m_1}}_{m_1} C^{\lambda_{m_2}}_{m_2} \ldots C^{\lambda_{m_n}}_{m_n} \Delta^{k-\lambda_1+\lambda_2+\ldots+\lambda_n}_{\lambda_{m_1}\lambda_{m_2}\ldots\lambda_{m_n}} \varphi(0, 0, \ldots, 0) \quad (23)$$

where $\phi(0, 0, \ldots, 0)$ is the value of the function ϕ for standard values of the discrete variables m^0_1, m^0_2, ..., m^0_n, $\Delta^k_{\lambda_{m_1}\lambda_{m_2}\ldots\lambda_{m_n}} \phi(0, 0, \ldots, 0)$ are finite differences, and $C^{\lambda_{m_1}}_{m_1}$, $C^{\lambda_{m_2}}_{m_2}$, ..., $C^{\lambda_{m_n}}_{m_n}$ are the numbers of the corresponding combinations.

Eqn.(23) is extremely cumbersome, but its application to calculations on polymers is facilitated by the fact that many macromolcules are linear sequences of isotypical atomic groups. As shown above, the properties of such polymers, starting from a fairly large average mass, cease to depend on the chain length, i.e. for certain average chain lengths the contribution of the end groups to the properties of the polymer is no longer appreciable. The thermodynamic properties of the polymer are in this case a function of the number and type of atoms or groups of atoms constituting the elementary structural chain units.

As an example, Pavlinov et al.[40] examined the vinyl series of polymers. An individual polymer chain of this series was represented in the form $-[-CH_{2-m_1}X_{m_1} - CH_{2-m_2}X_{m_2}-]-$, where X is a univalent substituent (X = H, Cl, CH_3, C_6H_5, etc.) and m_1 and m_2 are the numbers of substituents in the elementary unit (m_1, m_2 = 0, 1, 2; $m_1 \leq m_2$). In this case the properties of the polymer, referred to the elementary unit, are a function of only the two variables m_1 and m_2. Then, approximating to within second order differences, we have

$$\varphi(m_1, m_2) = \varphi(0, 0) + (m_1 + m_2)\,\Delta^1_{1,0}\varphi(0, 0) + \frac{1}{2}[m_1(m_1 - 1) + m_2(m_2 - 1)]\,\Delta^2_{2,0}\varphi(0, 0) + m_1 m_2 \Delta^2_{1,1}\varphi(0, 0). \quad (24)$$

Here the point (0, 0) corresponds to unsubstituted polyethylene and finite differences of the type

$$\begin{aligned} \Delta^1_{1,0}\varphi(0, 0) &= \Delta^1_{0,1}\varphi(0, 0) = \varphi(1, 0) - \varphi(0, 0), \\ \Delta^2_{1,1}\varphi(0, 0) &= \varphi(1, 1) - 2\varphi(1, 0) + \varphi(0, 0), \\ \Delta^2_{2,0}\varphi(0, 0) &= \Delta^2_{0,2}\varphi(0, 0) = \varphi(2, 0) - 2\varphi(1, 0) + \varphi(0, 0) \end{aligned} \quad (25)$$

correspond to different degrees of X-substitution of the polymer unit. It is more convenient to use Eqn.(24) in the form

$$\varphi(m_1, m_2) = \varphi_0 + (m_1 + m_2)\varphi_1 + (m_1 + m_2)^2\varphi_2 + m_1 m_2 \varphi_3, \quad (26)$$

where ϕ_0, ϕ_1, ϕ_2, and ϕ_3 are linear combinations of $\phi(0, 0)$, $\Delta^1_{1,0}\phi(0, 0)$, $\Delta^2_{1,0}\phi(0, 0)$, and $\Delta^2_{1,1}\phi(0, 0)$ of the type $\phi_0 = \phi(0, 0)$, $\phi_1 = \Delta^1_{1,0}\phi(0, 0) - \frac{1}{2}\Delta^2_{2,0}\phi(0, 0)$, $\phi_2 = \frac{1}{2}\Delta^2_{2,0}\cdot\phi(0, 0)$ and $\phi_3 = \Delta^2_{1,1}\phi(0, 0) - \Delta^2_{2,0}\phi(0, 0)$ characterising only the form of the substituent X.

If the order of the substitution in the formation of disubstituted polyethylene is immaterial, i.e. if $\Delta^2_{1,1}\phi(0, 0) = \Delta^2_{2,0}\phi(0, 0)$, then $\phi(m_1, m_2)$ can be represented in the form of a parabolic function of the total substitution number $l = m_1 + m_2$:

$$\varphi(m_1, m_2) = \varphi_0 + \varphi_1 l + \varphi_2 l^2 \quad (27)$$

In terms of their structure, Eqns.(24), (26), and (27) reflect the pair-additive approach of Bernstein.[1] With certain simplifications, it is easy to obtain on the basis of Eqns. (24), (26), and (27) a series of semiempirical schemes for

the calculation of the physicochemical properties of substances.[13,14,41–43]

Table 5. The results[40] representing in the form of the function $\phi(m_1, m_2) = \phi_0 + \phi_1 l + \phi_2 l^2$ the thermodynamic and kinetic experimental data[16,43,46,52] characterising X-substituted derivatives of polyethylene, their thermal decomposition processes, and the polmerisation of X-derivatives of ethylene.

φ	X	State	φ_0	φ_1	φ_2
ΔH^0_{form} (298), kJ mol^{-1}	Cl	S	−58.6*	−26.4*	1.7*
	Cl	G	−41.0	−26.8	−3.8
	F	S	−54.4*	−227.6*	9.6*
	F	G	−41.0	−187.0	0
	CH_3	S	−56.1	−38.9	11.3
		G	−41.0	−23.0	−3.8
S^0 (298), J mol^{-1}K^{-1}	Cl	S	47.7	15.5	2.1
	F	S	48.1	2.9	3.3
	CH_3	S	48.1	38.5	−7.1
C_p^0 (298), J mol^{-1}K^{-1}	Cl	S	49.0	5.4	5.9
	CH_3	S	49.0	51.9	−10.9
ΔH^0_{pol} (298), kJ mol^{-1}	Cl	L, S	−88.7	−20.9	13.8
	F	L, S	−88.7	−24.3	2.1
	CH_3	L, S	−88.7	−2.9	10.0
ΔS^0_{pol} (298), J mol^{-1}K^{-1}	Cl	G, S	−173.6	−0.8	−6.7
	Cl	L, S	−100.4	−17.8	5.2
	CH_3	G, S	−173.6	−15.9	2.1
$E_d^{\neq}$, kJ mol^{-1}	F	S, G	265.3*	−87.9*	25.9*
	CH_3	S, G	263.6	−12.6	−8.4
T_{hd}, °C	F	S, G	411.5*	−52.3*	18.8*
	CH_3	S, G	406.0	−9.0	−10.0

*The results have been obtained[40] by solving a system of three linear equations.
Note. G = gas, L = liquid, and S = solid (Ed.of Translation).

As a consequence of the insufficiency of literature data (see the relevant reviews[16,31,39,43–46]), thermodynamic characteristics of F-, Cl-, and CH_3-substituted polyethylene derivatives such as the enthalpy of formation, the entropy, and the heat capacity have been estimated[40] within the framework of the approximation defined by Eqn.(27). The constants ϕ_0, ϕ_1, and ϕ_2 required for the calculation (Table 5) were obtained in two ways. The first way consisted in solving a system of three linear algebraic equations using the known values of the thermodynamic parameter for all three X-substituted polyethylene derivatives (with l = 0, 1, 2, or l = 0, 2, 3). In this case the non-averaged constants ϕ_0, ϕ_1, and ϕ_2 were used to calculate the properties of the polymers; the calculations of $\phi(m_1, m_2)$ then fully reproduced the reference data despite the possibility of the inaccuracy of the former (see Table 6). In those cases where the number of equations exceeded the number of unknown constants (one property was investigated by different workers), the system was solved by the method of least squares, which yielded more accurate (average) coefficients ϕ_0, ϕ_1, and ϕ_2. Extrapolation of function (27) ("forward" and "backwards") made it possible to obtain the hitherto uninvestigated properties for two other degrees of substitution of the polymer (l = 3, 4 or l = 1, 4; Table 6).

Comparison of the difference terms ϕ_0, ϕ_1, and ϕ_2 (Table 5), found from the enthalpies of formation of F-, Cl-, and CH_3-substituted polyethylenes, corresponding repsectively to the condensed phase and the state of isolated chains shows that the transition of the polymer from the first physical state to the second alters most the quadratic term in the approximation equation (27). Relations of type (27) for the enthalpies of formation of F-substituted polyethylenes (in the gaseous state) and the entropies of Cl-substituted polyethylenes (in the solid state) and also for the enthalpies and entropies of

Table 6. Comparison with experimental data of the thermodynamic and kinetic quantities calculated[40] in terms of the quadratic approximation and characterising X-substituted polyethylenes, their thermal decomposition processes, and the polymerisation of X-substituted derivatives of ethylene.

l	$-\Delta H^0_{form}$ (298; S), kJ mol^{-1}		S^0 (298; S), J mol^{-1}K^{-1}		$-\Delta H^0_{pol}$ (298; L, S), kJ mol^{-1}		$-\Delta S^0_{pol}$ (298; G, S), J mol^{-1}K^{-1}		$-\Delta S^0_{pol}$ (298; L, S), J mol^{-1}K^{-1}		$E_d^{\neq}$ (S, G), kJ mol^{-1}		T_{hd}, °C (S, G)	
	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	(Ref.52)	calc.	(Ref.52)
						X = CH_3								
0	56.1	56.1 [53—55]	48.1	48.1 [46, 48]	88.7	87.7 [53]	173.6	173.6 [49]	100.4	100.4 [16]	264	264	406	406
1	83.7	83.7 [56]	79.5	79.5 [49]	81.6	81.6 [79]	187.4	187.4 [46]	116.3	116.3 [6]	243	243	387	387
2*	88.7	88.7 [55]	96.7	96.7 [50]	54.0	54.0 [80]	197.1	197.1 [46]	120.5	120.5 [6]	205	205	348	348
3	71.1	—	95.4	—	−5.9	—	202.5	—	113.0	—	151	—	289	—
4	31.0	—	88.3	—	−62.8	—	203.6	—	93.7	—	79	—	21	—
						X = Cl								
0	58.6	56.1 [53—55]	47.7	48.1 [46, 48]	88.7	88.7 [53]	173.6	173.6 [49]	100.4	100.4 [16]	—	—	—	—
1	83.7	81.2 [45, 47] 94.6 [61]	65.3	65.3 [46]	95.8	95.8 [61]	181.2	181.2 [46]	113.0	113.0 [46]	—	—	—	—
2*	104.6	100.4 [61]	83.7	87.0 [46]	75.3	75.3 [61]	202.5	202.5 [46]	115.0	115.1 [46]	—	—	—	—
3	121.8	—	110.5	—	27.2	—	237.7	—	106.7	—	—	—	—	—
4	135.6	—	146.0	—	−48.5	—	286.6	—	87.9	—	—	—	—	—
						X = F								
0	54.4	56.1 [53—55]	48.1	48.1 [46, 48]	88.7	88.7 [53]	—	173.6 [49]	—	100.4 [16]	264	264	411	406
1	272.4	267.8**	54.4	54.4**	111.3	—	—	—	—	—	205	—	378	389
2*	471.1	474.0 [62]	67.4	—	128.9	128.9 [62]	—	—	—	—	192	205	382	—
3	650.6	651.0**	87.0	—	144.3	—	—	—	—	—	234	222	423	413
4	810.9	809.6 [4]	113.4	113.4 [51]	154.8	154.8 [63]	—	197.1 [6]	—	118.1 [81]	331	335	503	509

*1,1-Disubstituted ethylene.
**Results obtained by Pavlinov et al.[40] using the method of linear correlations.
Note. G = gas, L = liquid, and S = solid [numbers in square brackets denote references (Ed.of Translation)].

polymerisation of F- and CH_3-derivatives of ethylene, corresponding to transitions of the type (liq.) → (solid) and (gas) → (solid), differ little from the linear relation, in contrast to the others examined in Table 5. Eqn.(27) can be linear only subject to the condition that $\Delta^2_{1,1}\phi(0, 0) = \Delta^2_{2,0}\phi(0, 0) = 0$. In this case there is a simple additive relation between the property and the degree of substitution:

$$\varphi(m_1, m_2) = \varphi_0 + \varphi_1 l. \qquad (28)$$

An analogous form of approximation has been used, for example, in Szabo's method of increments for C–C bonds.[41]

In this case, on comparing the properties of a series of derivatives of polyethylene with two types of substitution, namely $-[-CH_{2-}m_1\text{-}n_1X_{m_1}Y_{n_1}\text{-}CH_{2-}m_2\text{-}n_2X_{m_2}Y_{n_2}-]-$ (A) and $-[-CH_{2-}m_1X_{m_1}\text{-}CH_{2-}m_2X_{m_2}-]-$ (B), for which the variable factor is only the type of substituent X while the substitution numbers m_1, m_2, n_1, and n_2 and the type of substituent Y are fixed, it is possible to put forward, on the basis of Eqn.(27), a simple relation between the properties of the corresponding members of these series:

$$\varphi_A(X) = \Delta\varphi^0_{A,B} + \varphi_B(X), \qquad (29)$$

because

$$\Delta\varphi^0_{A,B} = \varphi_A(0) - \varphi_B(0) + (\varphi^A_{1,A} - \varphi_{1,B})\,l + (\varphi_{2,A} - \varphi_{2,B})\,l^2 + m_1m_2(\varphi_{3,A} - \varphi_{2,B}) = \text{const}.$$

Eqn.(29) reproduces the rule of constant differences for the properties of isotypical substances formulated by Karapet'yants.[13] Its applicability to vinyl polymers has been confirmed[40] with the aid of pair-correlation analysis.[20] Examination of the relations between the thermodynamic parameters [$\Delta H^0_{form}(298)$ and $S^0(298)$] of two groups of vinyl polymers of the type $-[-CH_2-C(CH_3)X-]-$ and $-[-CH_2-CHX-]-$ with different substituents X (H, CH_3, COOH, $COOCH_3$, and C_6H_5) showed[40] that they are linear with a fiducial probability $P \geq 0.999$ and a probable correlation error $\alpha \leq 0.1\%$. Their linear correlation coefficients are in the range 0.98–0.99. Relations of this kind also make it possible in many instances to estimate thermodynamic parameters where experimental data either do not exist or are difficult to determine.

The application of the interpolation method when the dependence of the thermodynamic and kinetic parameters of polymerisation reactions of the ethylene derivatives $CH_{2-}m_1X_{m_1} = CH_{2-}m_2X_{m_2}$ on the number or type of substituents X is considered merits particular attention. In relation to polymerisation reactions, Eqns.(26) and (27) can be written in an analogous form for both thermodynamic and kinetic reaction parameters, since the number and type of substituents per mole of the monomer which has reacted or been activated do not change in this process.

The parabolic function (27) describes fairly adequately the dependence of the enthalpies and entropies of polymerisation of F-, Cl-, and CH_3-substituted ethylenes on the number l (Table 6). On the basis of the relations $\Delta H^0_{pol} = f(l)$ and $\Delta S^0_{pol} = \phi(l)$ obtained in this way (Table 6), it has been shown[40] that the polymerisation of ethylene derivatives containing three (and, even more so, four) substituents of the type of Cl and CH_3 is thermodynamically unfavourable even at room temperature (298 K), since $\Delta G^0_{pol} = \Delta H^0_{pol} - 298\Delta S^0_{pol} > 0$. At higher temperatures the thermodynamic prohibition of the polymerisation of these systems becomes even more stringent. Judging from the available experimental data (see the relvant reviews[16,46]) and the data in Table 6, the polymerisation of F-substituted ethylenes is thermodynamically allowed for all degrees of substitution of ethylene, because different values of l (1, 2, 3, 4) give high negative values of ΔG^0_{pol}.

The attempt to use the method of finite differences for a quantitative description of the kinetic parameters of a process as complex as the thermal decomposition of compounds of the vinyl series, involving the rupture of the principal bonds, is also of interest.[44,52] The activation energies $E^{\neq}_a$ and half-decomposition temperatures T_{hd} of a series of F- and CH_3-substituted polyethylenes[52] are described by the parabolic function (27) (Table 6) to within several per cent, which corresponds to the experimental error in the determination of these quantities. The parallel variation of $E^{\neq}_a$ and T_{hd} as a function of l in the case of the same substituent can be seen from Tables 5 and 6. The character of the variation of the thermal stability of the polymers with increase of l observed under these conditions in the main confirms the conclusions reached in a study[40] of the thermodynamics of the polymerisation of F- and CH_3-substituted ethylenes.

Thus the difference interpolation method yields a fully correct idea about the character of the changes in the properties of the simplest polymer systems as a function of the number and type of side substituents in the chain.

6. Thermodynamic Properties of Polyheteroarylenes

The modelling methods described above can be successfully employed to calculate the thermodynamic parameters not only of polymers with a simple chemical structure but also of complex systems such as polyheteroarylenes.[19] The attempts at an exact determination of the heats of formation of these polycondensation polymers directly with the aid of combustion calorimetry as a rule encounter serious difficulties.[82–88] On the other hand, the application of reaction calorimetry also does not always achieve this aim[18,19] as a consequence of the complexity of the synthesis of the above systems (sometimes involving a multistage process). By virtue of the competition between the main polycondensation reaction of the starting materials with various secondary reaction pathways, many of the rigid-chain polyheteroarylenes have a "heterounit" structure of the macromolecules, i.e. contain an appreciable amount of chemically defective structural fragments.[19,89,90] For example, in the two-stage synthesis of polyheteroarylenes, where polyfunctional amines and dianhydrides (dichlorides) of aromatic di- or tetra-carboxylic acids are used as the starting materials, the final polycondensation products are usually infusible and insoluble substances containing complex combinations of the fragments of the initial, intermediate, and final polymeric structures.[89,90] For this reason, the experimental thermodynamic characteristics of polyheteroarylenes usually require more fundamental checks with the aid of phenomenological computational methods than the analogous characteristics of other less complex polymers.

The thermodynamic properties of polyheteroarylenes have now been calculated so far in only one study[19] with the aid of the method based on the linear correlation of properties in model–polymer systems (Table 7). In the determination of the enthalpies of formation of polyheteroarylenes in the above investigation, the simplest version of the correlation method, namely the rule of constant differences between the properties of isotypical polymers (P_i) and model substances (M_i), was employed. In conformity with this rule, it was assumed that $\beta = 1$ and $\Delta(\Delta H^0_{form}) = \text{const}$. (corresponds to a constant increment in the end groups R^1 and R^2 of the models M_i) in the expression

$$\Delta H^0_{form}(298, P_i) = \Delta(\Delta H^0_{form}) + \beta \cdot \Delta H^0_{form}(298, M_i) \qquad (30)$$

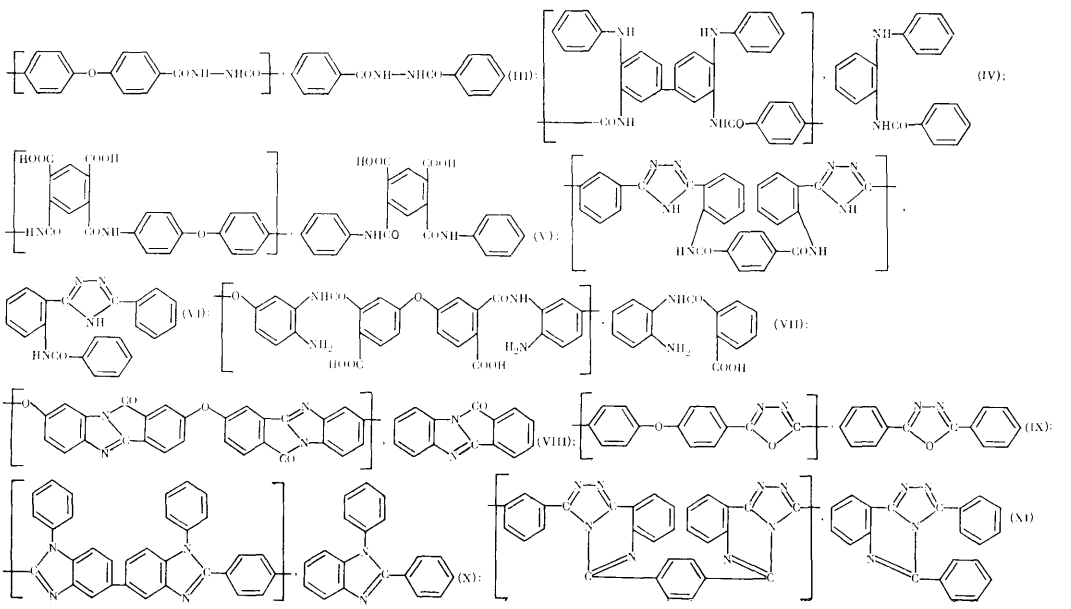
It has already been stated that this approach yields a probable correlation error less than 1% for vinyl polymers. In an approach of this kind the calculation of the enthalpy of formation of an individual polyheteroarylene can be achieved knowing only the difference between the heats of formation $\Delta(\Delta H^0_{form})$ for a reference polymer–model pair and the heat of formation of the model corresponding to the polyheteroarylene. The authors[19] chose as the reference pairs various derivatives of poly-*p*-phenylene and the corresponding aromatic compounds, while the models chosen for polyheteroarylenes were compounds already investigated thermochemically[82–88] and the data for poly-*p*-phenylene were obtained[19] by extrapolating the properties in the polymer-analogue series of compounds with $n = 1, 2, 3$.

The results of such calculations are presented in Table 7, where the following designations for the polymer–model (P_i, M_i) correlation pairs were used:

Table 7. The enthalpies of formation of polyheteroarylenes (kJ mol^{-1}).

Correlation pair (P_i, M_i)	Phase	ΔH^0_{form} (298, M)	ΔH^0_{form} (298, P)	ΔH^0_{form} (298, P)	Method
		modelling (Ref.19)		experiment	
(III)	L	—	—		—
	Am-Cr	—	—	−307.9 [82]	R
	Cr	−201.7 [82]	−312.1	—	—
(IV)	L	39.7 [84]	52.3	—	—
	Am-Cr	—	—	65.7 [85] 110.9 [84]	R
	Cr	−9.6 [83]	−36.8	—	—
(V)	L	—	—	—	—
	Am-Cr	—	—	−1039.3 [85]	R
	Cr	−907.9 [85]	−1018.4	—	—
(VI)	L	—	—	—	—
	Am-Cr	—	—	199.6 [86]	R
	Cr	94.6 [86]	110.5	—	—
(VII)	L	—	—	—	—
	Am-Cr	—	—	−935.5 [87, 88]	CC
	Cr	−481.2 [87]	−1184.9	—	—
(VIII)	L	—	—	—	—
	Am-Cr	—	—	270.3 [87, 88]	CC + D
	Cr	66.9 [87]	−87.0	—	—
(IX)	L	—	—	—	—
	Am-Cr	—	—	6.7 [82]	R + D
	Cr	75.7 [82]	−34.7	—	—
(X)	L	324.7 [84]	621.7	—	—
	Am-Cr	—	—	641.0 [83]; 709.2 [84]	R + D
	Cr	296.6 [84]	575.3	—	—
(XI)	L	433.5 [84]	769.0	—	—
	Am-Cr	—	—	795.4 [86]	R + D
	Cr	399.2 [84]	719.6	—	—

Notation. CC is combustion calorimetry, CC + D is the combustion method combined with the study of the dehydration pressure, R is reaction calorimetry, R + D is the method of reaction calorimetry combined with the study of the dehydration pressure.
Note. L = liquid, Am-Cr = amorphous-crystalline, Cr = crystalline. The numbers in square brackets denote references (Ed.of Translation).



The authors[19] suggest that, by comparing the heats of combustion and formation of polyheteroarylenes calculated in this way by the modelling method and found experimentally, it is possible not only to eliminate certain erroneous experimental data but also to estimate the degree of defectiveness of the chemical structures of the polymer studied. However, one should note that both these problems have a solution only when fairly reliable thermochemical data are available for the individual compounds modelling the repeating fragments in the structures of the polyheteroarylenes, because the accuracy of the calculated characteristics of polymers is determined primarily by the accuracy of the experimental data for the models themselves.

Table 7 compares the experimental[82–88] and calculated[19] enthalpies of formation of nine polyheteroarylenes. The results of the calculations refer to two limiting phase states of the polymers—liquid (three polymers) and crystalline (nine polymers) and the experimental values refer in all cases to an undefined amorphous-crystalline state which in the case of polymers of this kind usually corresponds to an amorphous structure of the specimen and is designated by the authors[82–88] as the solid or condensed phase. For three of the nine polyheteroarylenes indicated in Table 7 (Entries No.2, 8, and 9), the discrepancies between the experimental[83,85,86] and calculated[19] heats of formation for the corresponding liquid-amorphous states lie within a narrow range (13–26 kJ mol^{-1}), which differs little from the range of experimental errors in the heats of formation of these polymers.

However, two additional experimental results,[84] presented in Table 7 for poly[*N*-terephthaloylbis(*N'*-*o*-phenylenediamine)] (No.2) and poly[2,2'-(*p*-phenylene)-1,1'-diphenyl-5,5'-dibenzimidazole] (No.8) can hardly be regarded as correct, as can be seen from their comparison with other experimental data[83] and calculated results. In all the remaining cases the data obtained by the modelling method refer solely to the crystalline polymer and the experimental quantities refer to an undefined amorphous-crystalline state. For this reason, certain difficulties arise in their comparison. Naturally, the difficulties can be partly obviated by estimating with the aid of Bondi's empirical rule ($\Delta H^0_{fu}/T_{fu} = 12.55 + 0.46V_m$, where V_m is the molecular volume) the heats of fusion of the models and then carrying out a rough estimate by Eqn.(30) of the corresponding heats of fusion of the polymers. According to this estimate, the changes in the heats of fusion of the group of nine polyheteroarylenes considered are in the range 40–80 kJ mol^{-1}. Since the observed discrepancies between the experimental and calculated heats of formation of four of the nine polymers (Nos.1, 3, 4, and 7, Table 7) fall within the above range, the discrepancies can probably be accounted for by the influence of the difference between the phase states of the polymers compared and in the case of polyhydrazide (No.1) and poly(*p*,*p'*-diphenyl oxide)pyromellitic acid amide (No.3) relatively small discrepancies in the given characteristics may actually indicate a certain amount of order in the real polymer structures.

Since in the case of the poly-*o*-aminoamidoacid (No.5) and pyrrone (No.6) discrepancies between the experimental and calculated enthalpies of formation exceed severalfold (by a factor of 3–4) the upper limit of the above range of heats of fusion, the authors[19] actually attributed them to the influence of the chemical defectiveness, which had not been taken into account, on the properties of real polymer structures. They actually used this factor to estimate the degree of defectiveness of the chemical structure of the poly-*o*-aminoamidoacid. Korshak and co-workers[19] made an approximate estimate of the content of defective structural elements in the real specimen of the poly-*o*-aminoamidoacid from its heat of combustion[87,88] and the heats of combustion (formation) calculated by the modelling method for pure poly-*o*-aminoamidoacid and poly-*o*-aminoimide (the main types of chemical defects in the initial polymer). It was found that the content of the main homopolymer units in the specimen was only 70 wt.% and that of the "extraneous" poly-*o*-aminoimide units was 30 wt.%.

Comparison of the different experimental procedures for the determination of the enthalpies of formation of polyheteroarylenes with the aid of the data in Table 7 shows that the most reliable method for the determination of this characteristic of polymers, synthesised by a single-state polycondensation process, involves calorimetric study of the synthetic reactions of the given systems. Combustion calorimetry yields in this instance less reliable results. For those polyheteroarylenes which are the products of the thermal cyclodehydration of the initial polycondensation polymers (two-stage synthesis), the best results are obtained via a two-stage method for thermodynamic studies involving the application of combustion calorimetry in the first stage. For this reason, in order to estimate the heat of formation of the initial polyfunctional polymer, in a number of studies[82,83,86] the authors were forced to investigate calorimetrically the synthesis of the polymer and also the thermodynamic characteristics of the corresponding reactants. The temperature dependence of the cyclodehydration pressure of the initial polymer was determined in the second stage, which made it possible to find the enthalpy of the cyclodehydration process. The enthalpy of formation of the final product was then determined with the aid of Hess's cycle taking into account the enthalpies of the intermediate processes.

Thus the data considered above show that, together with the traditional classical phenomenological methods for the calculation of the thermodynamic properties of polymers, it is nowadays possible to employ successfully methods involving their modelling on the basis of data obtained for low-molecular-weight analogues. Different versions of these methods (the method of linear correlations of properties, the method of the difference interpolation of the properties of substituted polymers, and certain versions of the method of extrapolation of properties in polymer-analogue series of compounds) are sufficiently exact and universal.

On the basis of the methods indicated, it is possible to predict successfully the thermodynamic parameters not only of polymers with a simple chemical structure but also of relatively complex polyconjugated structures, namely aromatic polymers and polyheteroarylenes, to which is has so far been impossible to apply any other known approaches. The modelling methods can also be used to calculate the bond strengths in polymer macromolecules and to predict their thermal stability.

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Kalinin State University

Translated from *Uspekhi Khimii*, 53, 1197-1221 (1984) U.D.C. 541.6+536.46

Spinodal Decomposition in Polymeric Systems

Yu.S.Lipatov and V.V.Shilov

The characteristics of the phase separation in multicomponent systems in the region of unstable states are considered using the formal treatment of Cahn and Hilliard. The general theories of spinodal decomposition developed recently are briefly discussed. The characteristic features of systems based on high-molecular-weight components are analysed from the standpoint of phase separation using the Debye-van Aartsen relations. The theory of spinodal decomposition developed by de Gennes and Pincus for mixtures based on two homopolymers is examined in detail. The principal results obtained in experimental studies of phase separation of the liquid-liquid type in polymer-solvent and polymer-polymer systems are presented. The possibilities in the application of the concept of spinodal decomposition to a wider range of complex multicomponent systems as well as the results obtained recently by the authors of the review in the study of phase separation in systems of this kind are discussed. The attempts at the analysis of the spinodal decomposition phenomena within the framework of the non-linear thermodynamics of irreversible processes developed by Prigogine are considered.
The bibliography includes 89 references.

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I. INTRODUCTION

It is known that, depending on the character of the interaction of the components, binary systems can consist of one or two phases. If a system of this kind consists of only one phase, microregions with a non-homogeneous decomposition of the components, namely composition fluctuations, exist in it. After time intervals of the order of magnitude of the duration of diffusional jumps, such fluctuations are spontaneously generated or dissipated. A characteristic feature on the basis of which a particular system can be classified as a one-phase system, is the presence of an equilibrium distribution of fluctuations.[1] Such a distribution is fully controlled by external conditions and the composition of the system and is independent of time. At the same time, there exist two-phase systems with a high degree of dispersion which are outwardly similar to the one-phase systems. The principal difference between the former systems and one-phase systems is the absence of an equilibrium distribution of microregions of inhomogeneity.

An important difference between one- and two-phase systems also consists in the fact that in the latter systems the microregions of inhomogeneity consist of microvolumes with the properties of pure phases. In principle, the size of such microregions can increase with time until the complete separation of the system into layers. The transition from a one-phase system to a two-phase system is attributed to an enhancement of the intensity of the composition fluctuations and the development of their basis of microregions of new phases. This takes place when the system is in a metastable region (between the binodal and the spinodal) or in an unstable region (within the spinodal) of the phase diagram.

The classical approach to the problem of the stability of phases has been developed by Gibbs.[2] According to Gibbs, the most characteristic points on the free energy—concentration relation $G(c)$ are points of inflexion at which the sign of the second derivative changes. When the condition $\partial^2 G/\partial c^2 > 0$ holds, the diffusion fluxes of the components are directed towards a diminution of the composition fluctuations, while under the condition $\partial^2 G/\partial c^2 < 0$ the directions of the diffusion fluxes are reversed. In this case the intensity of the composition fluctuations in the system increases—as a one-phase system it becomes unstable and should decompose spontaneously into regions with equilibrium compositions. The region of unstable states is bounded on the phase diagram by a curve called the spinodal. On the "outer" side, the region of metastable states bounded by the binodal adjoins the spinodal. In this region, as in the case of a one-phase binary system, the diffusion fluxes of the components are directed towards the diminution of the composition fluctuations. Nevertheless, the segregation of a new phase begins precisely in this part of the diagram. Under these conditions, the occurrence of the energetically unfavourable effect involving the formation of an interface makes the system unstable only in relation to fluctuations whose dimensions are greater than the critical value and the fluctuations themselves have a composition similar to that of the new phase. Such fluctuations are called critical nuclei.

The appearance of such critical nuclei in an A + B mixture, for example nuclei based on component A, leads to the formation around the nucleus of a zone depleted in component A. The diffusion fluxes tend to make good the resulting deficiency and at the same time feed the nucleus which has been formed. This is responsible for the continuous growth of the microvolumes of the new phase. In this

case phase separation proceeds via a mechanism involving nucleation and growth. A characteristic feature of the "classical" theories of nucleation is that the critical nucleus is regarded as a microscopic drop of a pure new phase. The treatment of the kinetic aspects of the appearance, growth, and coalescence of the microregions of the segregated phase within the bulk of the homogeneous solution in the region of metastable states is based on this hypothesis.[3]

A general approach to phase separation in inhomogeneous systems has been developed in the studies of van der Waals, Hart, Cahn and Hilliard.[4-11] The theory of spinodal decomposition in solution developed by Cahn and Hilliard has proved particularly fruitful[7-11] and has been confirmed experimentally by numerous data on phase separation in metallic alloys and inorganic glasses.[12,13] In particular, Cahn and Hilliard have established that the critical nuclei formed on nucleation in the metastable state can differ significantly in their composition from the particles of the new phase.[8] In the immediate vicinity of the binodal, critical nuclei are formed whose composition, radii, and interfaces are indeed close to the characteristics of the classical nuclei of the new phase. However, as the spinodal is approached, the deviations of the concentration in the nuclei from that in the initial solution become smaller to an increasing extent, the radii of the nuclei become increasingly larger, and the work of their formation approaches zero.

II. THEORETICAL IDEAS CONCERNING PHASE SEPARATION IN BINARY SYSTEMS VIA THE SPINODAL MECHANISM

According to the ideas developed by Cahn and Hilliard,[6-8] the free energy of a binary system with small composition fluctuations can be formulated as follows in terms of a linear approximation:

$$F = \int_v [f(c) + k(\nabla c^2)]\,dv \,, \qquad (1)$$

where $f(c)$ is the density of the free energy of the homogeneous system in which the concentration of component A is c and $k(\nabla c)^2$ is the "gradient energy", which represents the first term in the expansion of the free energy, describing its increase as a result of the appearance of the concentration (composition) gradient. Taking into account the expansion of $f(c)$ in terms of the average concentration c_0, the difference between the free energies of the inhomogeneous system and the initial homogeneous solution is

$$\Delta F = \int_v \left[\frac{1}{2}\left(\frac{\partial^2 f}{\partial c^2}\right)_{c_0}(c-c_0)^2 + k(\nabla c)^2\right] dv \,. \qquad (2)$$

Bearing in mind that the quantity $k(\nabla c)^2$ is always positive, the condition for the instability of the system in relation to small composition fluctuations can be written as follows.

$$\partial^2 f/\partial c^2 < 0 \,. \qquad (3)$$

For composition fluctuations corresponding to a periodic variation of the density along the coordinate x, we have

$$c - c_0 = A\cos(qx) \,, \qquad (4)$$

where A is a constant factor and q the wave vector. The sum of such fluctuations for different periods, representing the sum of the Fourier components in the expansion of the concentration, can be regarded as the local difference between the concentrations. The contribution of the component with the wavelength $2\pi/q$ in the relation for the free energy change as a result of composition fluctuations is

$$\frac{1}{4}VA^2\left[\left(\frac{\partial^2 f}{\partial c^2}\right) + 2kq^2\right] \,, \qquad (5)$$

where V is the volume of the system.

When condition (3) holds, the contribution of an expression of type (5) to ΔF becomes negative if the wavelength of the Fourier component reaches the critical value λ_c defined by the expression

$$q_c = \left(-\frac{\partial^2 f}{\partial c^2}\cdot\frac{1}{2k}\right) \,. \qquad (6)$$

In the initial stages of spinodal decomposition, where the linear approximation of the Cahn–Hilliard theory [Eqn.(1)] is valid, the difference between the local chemical potentials of the components can be represented in the form[9]

$$\mu_A - \mu_B = \left(\frac{\partial F}{\delta C_A}\right) - \left(\frac{\partial f}{\partial c_A}\right) - 2k\nabla^2 c_A \,. \qquad (7)$$

In this case the diffusion fluxes of the components are expressed by the relation

$$J_A = -J_B = M\nabla(\mu_A - \mu_B) \,, \qquad (8)$$

where M is a phenomenological coefficient characterising the diffusional mobility of the components. Using the relations presented, the diffusion equation can be reduced to the form

$$\partial c/\partial t = M(\partial^2 f/\partial c^2)\nabla^2 c - 2Mk\nabla^4 c \,. \qquad (9)$$

The coefficient of $\nabla^2 c$ is the diffusion coefficient.

Thus, in contrast to Fick's Second Law, Eqn.(9) contains a term proportional to $\nabla^4 c$. On the spinodal, the diffusion coefficient changes sign, which leads to an enhancement of the composition fluctuations characteristic of spinodal decomposition. Under these conditions, phase separation is initiated by the selective growth of sinusoidal composition fluctuations and takes place on the basis of microregions with small deviations from the composition of the equilibrium solution. The solution of the diffusion equation yields the time variation of the local concentration difference $c - c_0$:

$$c - c_0 = \exp[R(q)t]\cdot\cos(qx) \,, \qquad (10)$$

where $R(q)$ in the exponent represents the so-called amplification factor:

$$R(q) = -Mq^2(1+2q^2). \qquad (11)$$

It is seen from Eqn.(5) that, when $q > q_c$, we have the factor $R(q) < 0$ and consequently the concentration difference diminishes with time. This corresponds to the decay of the composition fluctuations. On the other hand, when $q < q_c$, the quantity $R(q)$ becomes positive and the concentration difference increases with time. The amplification factor has a maximum when

$$q_m = \frac{1}{2}\left[-\left(\frac{\partial^2 f}{\partial c^2}\right)/k\right]^{1/2} \,. \qquad (12)$$

For the maximum value of $R(q)$, a sharp maximum is obtained in the quantity $c - c_0$ specified by Eqn.(10). In the general solution of the diffusion equation one can therefore neglect all the components of the Fourier expansion of the difference $c - c_0$ except that which corresponds to q_m.

Thus in the initial stages of the spinodal decomposition, an exponential increase of the intensity of the composition fluctuations, whose wavelength is defined by Eqn.(12), is observed. The following equation holds between the optimum and critical wavelengths of spinodal decomposition:[9]

$$\lambda_m = \sqrt{2}\lambda_c \,. \qquad (13)$$

For later stages of the spinodal decomposition, i.e. with increase of $c - c_0$, Eqn.(1) becomes a rough approximation, since a continuous increase of $c - c_0$ with time follows from it. In fact the concentration difference cannot exceed a limiting value corresponding to the segregation of microregions of the pure components.

It has been shown[14] that the diffusion equation for later stages of spinodal decomposition becomes

$$\partial c/\partial t = D_1\nabla^2 c - D_2\nabla^4 c + D_1'(\nabla c)^2 + D_n \quad (14)$$

where

$$D_1 = \frac{M}{N_v}\left[\frac{\partial^2 f}{\partial c^2}\right];\ D_2 = 2Mk/N_v;\ D_1' = \partial D_1/\partial c$$

(N_v is the number of atoms per unit volume) and D_n is a higher-order non-linear expression.

In those cases where the volume of the system depends on its composition, the sequence of infinitesimal composition fluctuations in the solid should lead to the appearance of elastic deformations.[11] It has been shown that this results in the appearance of an additional contribution to the free energy of the system described by the expression[10,11]

$$\eta^2 E(c - c_0)^2/(1 - \nu) \quad (15)$$

where E is Young's modulus, ν the Poisson coefficient, and η the linear expansion corresponding to a unit change in the composition. When account is taken of this relation, the contribution of the Fourier component with a wavelength $2\pi/q_m$ to ΔF can be represented by the expression

$$\frac{1}{2}VA^2\left[\left(\frac{\partial^2 f}{\partial c^2}\right) + \frac{2\eta^2 E}{1 - \nu} + 2kq^2\right] \quad (16)$$

Consequently, for a system with elastic deformations resulting from the local change in composition, the limit of stability is defined by the condition

$$\partial^2 f/\partial c^2 + Y = 0 \quad (17)$$

where $Y = 2\eta^2 E/(1 - \nu)$.

Thus elastic stresses stabilise the system. Eqn.(17) yields the position of the so-called coherent spinodal, in contrast to the "chemical" spinodal determined solely by the chemical nature of the components and expressed by the conditions $\partial^2 f/\partial c^2 = 0$.

Cahn's theory nowadays continues to be the main one employed in the study of the kinetics of phase separation via the spinodal mechanism in ageing metallic alloys,[12] in inorganic glasses,[13] etc. The corresponding experiments are based on the application of methods of the low-angle scattering of X-rays.

The application of the Cahn–Hilliard theory to the interpretation of experimental data for the scattering of radiation makes it possible to obtain characteristics such as the optimum and critical wavelengths of the spinodal decomposition, the second derivative of the free energy with respect to composition, the quantities $\eta^2 E/(1 - \nu)$ (if elastic stresses arise in the system), and k in Eqn.(1). The calculations carried out for this purpose are based on the analysis of the time variation of the intensity of X-ray scattering in the region of the diffraction maximum. It has been shown[15] that this variation is defined by the relation

$$I(q, t) = I(q, 0)\exp[2R(q)t] \quad (18)$$

where

$$R(q) = -(D/f'')(f'' + 2\eta^2 E/(1 - \nu) + 2kq^2)q^2 \quad (19)$$

(D is the mutual diffusion coefficient for the components). It follows from the theory that the following main features of spinodal decomposition can be isolated: (1) the linear dependence of the logarithm of the intensity of the scattered radiation on time; (2) the linear dependence of $R(q)/q^2$ on q^2; (3) the presence of an interference maximum in the relation between the intensity of the scattered radiation and the angle. The manifestation of these effects makes it possible to reach a qualitative conclusion concerning the presence or absence of spinodal decomposition and analysis of the corresponding relations permits the determination of the most important characteristics.

It follows from Eqn.(18) that the slope of the linear relation $\ln[I(q, t)] = \phi(t)$ yields $R(q)$. It it is positive, the composition fluctuations in the system are enhanced, i.e. separation via the spinodal mechanism takes place. The quantity $(-2kD/f'')$ can be determined from the slope of the plot of $R(q)/q^2$ against q^2 and $\{-D[1 + 2\eta^2 E/(1 - \nu)f'']\}$ can be estimated from the intercept which the straight line makes on the ordinate axis. Thus all the quantities characterising the phase separation can be obtained for the initial stages of spinodal decomposition.

In the determination of the most characteristic features of spinodal decomposition, studies on the mathematical modelling of phase separation in the region of unstable states on the phase diagram have played a major role. Despite the comparatively small number of such investigations, their results have proved extremely instructive, because they make it possible to follow the appearance, enrichment, and in certain individual instances also the coalescence of the microregions of the heterogeneous structure as a function of time.[16,17] In particular, it has been shown[17] that, for a definite composition of the system, there is a temperature corresponding to the maximum rate of formation of interrelated microregions of the phase separation. In this case the formation of modulated structures in spinodal decomposition corresponds to a comparatively brief period of the development of interacting nuclei. In the course of later stages of the decomposition, hydrodynamically initiated coalescence begins to play an important role. The possibility of modelling the process of phase separation in both the metastable and unstable regions of the phase diagram and also the possibility of obtaining information about the coalescence of the microregions at later stages of the decomposition[17] must be regarded as a significant characteristic of the results obtained in the numerical soluton of a diffusion equation of type (14).

A series of theoretical studies whose aim was a more general description of the phenomenon of spinodal decomposition than had been achieved on the basis of the Cahn–Hilliard theory have appeared recently. The necessity for a more general approach to the analysis of phenomena arising in spinodal decomposition is associated primarily with the fact that the fundamental equation in the given theory [an equation of type (1)] is inapplicable in the general case because, for reasons involving symmetry considerations, it does not take into account contributions proportional to ∇c. A theory[18] based on a set of phenomenological coefficients determined from the conditions for correlation with experimental data has been proposed as one of the alternative formulations of the theory for the description of phase separation in the region of unstable states on the phase diagram.

Another approach developed recently is based on the extension of the perturbation theory for the liquid state to the case of inhomogeneous liquids.[19] The numerical solution of the corresponding diffusion equation, this time for the one-dimensional case, reveals appreciable deviations from the Cahn–Hilliard theory outside the linear regime.

One of the most rigorous versions of the modern theory of phase separation, including the description of nucleation and spinodal decomposition processes, has been developed

by Metiu et al.[20] and Varea and Rodledo.[21] It is based on the consideration of these processes as relaxation phenomena obeying the Markov equation. For a thermodynamic system with such a relaxation process (for example for a liquid in a specified state), the rate of change of the local density $\rho(r, t)$ is defined by the following evolution equation:

$$\frac{\partial \rho(r, t)}{\partial t} = -K\left[1 - \exp\left(\lambda^2\nabla^2/r\right)\frac{\partial\Omega}{\delta\rho(r)}\Big|_{\rho(r,t)}\right], \qquad (20)$$

where K is a constant related to temperature and to the characteristic time of the transitions, Ω the grand thermodynamic potential, and λ the distance traversed by the molecule of the liquid during the characteristic time.

Eqn.(20) describes the rate of the most probable evolution of density fluctuations. In terms of the approximation assuming a small variation in $\rho(r, t)$ compared with λ, the equation first obtained by Cahn[10] is valid:

$$\frac{\partial\rho}{\partial t} = K'\nabla^2\frac{\delta\Omega}{\delta\rho(r)}\Big|_{\rho(r,t)}. \qquad (20')$$

Analysis of Eqns.(20) and (20') shows that $\Omega[\rho(r)]$ can be identified with Lyapunov's function. Here the study of the number and properties of the corresponding stationary solutions is of special interest. The direction of the most probable evolution of this system is defined by the condition

$$\frac{d}{dt}\Omega[\rho(r, t)] \leqslant 0 .$$

In particular, if we have two stationary states $\rho_1(r)$ and $\rho_2(r)$, then on the path from the first to the second, the following condition is valid for the $\Delta\rho(r)$ fluctuation:

$$\Omega[\rho_1(r) + \Delta\rho(r)] > \Omega[\rho_2(r)] .$$

The stationary states are then defined by the condition:

$$\frac{\delta\Omega}{\delta\rho(r)} = \frac{\delta\Omega}{\delta\rho(r)} - \mu = 0 . \qquad (21)$$

Homogeneous states correspond to the trivial solution $\rho(r) = \rho$ of Eqn.(21). At the point where the trivial solution becomes unstable, a branching or bifurcation takes place.

Eqn.(21) yields the condition for the instability of each homogeneous solution in the spinodal region, i.e. an infinite family of inhomogeneous stationary states branches out from each point within the spinodal. The instabilities of the homogeneous solutions are determined either in terms of a mechanical analogy (a large response to an external influence) or in terms of a thermodynamic analogy {the absence of an unambiguously defined minimum in $\Omega[\rho(r)]$}. It has been established that periodic stationary states branch with a specific initial wavelength λ_c. A series of spontaneous fluctuations can cause a transition of the system from the homogeneous state which has become unstable, via the periodic states indicated, to a metastable state. Subsequently there is a possibility of a transition via nucleation from the metastable state to an equilibrium homogeneous state. Regarded as the Lyapunov function (20), the property $\Omega[\rho(r)]$ defines the direction in the sequence of stationary states traversed along the most probable path after the transition to the spinodal region of the phase diagram.

Thus the phenomenon of spinodal decomposition is associated with a large number of pathways whereby the system relaxes to equilibrium. In all cases, after quenching the system develops a periodic inhomogeneity, whose wave vector corresponds to the initial state; after a time, this inhomogeneity increases in amplitude and in wavelength until nucleation begins following the attainment of the metastable state. It has been shown[21] that in this state the fluctuations in different regions of space are independent. Such fluctuations lead to the development of a nucleation process which cannot be described within the framework of the local Cahn–Hilliard approximation.

III. APPLICATION OF THE THEORY OF SPINODAL DECOMPOSITION TO SYSTEMS BASED ON HIGH-MOLECULAR-WEIGHT COMPONENTS

The majority of investigations of phase separation in systems based on high-molecular-weight components are themselves based on the familiar study by Debye[22] devoted to critical opalescence. The relations obtained by Debye for a few systems are in essence analogous to the results of the studies of Cahn and Hilliard examined above. Debye used the following expression for the free energy of a binary system:

$$F = k_BT\int_v d\upsilon\left[\left\{\frac{\varphi_A^0}{\omega_A}\ln\varphi_A^0 + \frac{(1-\varphi_A^0)}{\omega_B}\ln(1-\varphi_A^0) + \right.\right.$$
$$\left.\left. + \frac{\Omega}{2k_BT}\varphi_A^0(1-\varphi_A^0)\right\} + \left(\frac{1}{\omega_A\varphi_A^0} + \frac{1}{\omega_B\varphi_B^0} - \frac{\Omega}{k_BT}\right)\frac{\eta^2}{2} + \frac{H}{2k_BT}(\nabla\eta)^2\right], \qquad (22)$$

where ϕ_A^0 is the volume fraction of component A, ω_A the volume occupied by the molecule of A, ϕ_A the local value of ϕ, $\eta = \phi_A - \phi_A^0$, and

$$\Omega = W_{AA}|\omega_A^2 + W_{BB}|\omega_B^2 - 2W_{AB}|\omega_A\omega_B ,$$
$$H = \frac{1}{6}\left[\frac{W_{AA}}{\omega_A^2}l_{AA}^2 + \frac{W_{BB}}{\omega_B^2}l_{BB}^2 - 2\frac{W_{AB}}{\omega_A\omega_B}l_{AB}^2\right] .$$

The quantities Ω and H are the interaction parameters. Here we have

$$W_{AA} = \int\varepsilon_{AA}d\upsilon,\ W_{AA}l_{AA}^2 = \int r^2\varepsilon_{AA}d\upsilon,$$
$$l_{AA}^2 = \int r^2\varepsilon_{AA}d\upsilon\Big/\int\varepsilon_{AA}d\upsilon$$

where $-\varepsilon_{AA}$ is the energy of the A–A interaction between the molecules and l_{AA} the characteristic distance of the interaction between these molecules.

On the basis of the relations presented above, the contribution to the free energy of the system associated with the inhomogeneous distribution of the components can be represented in the form

$$\Delta F = \int d\upsilon\left[\frac{1}{2}\left\{\frac{\partial^2F_m/V}{\partial^2\varphi_A^2}\right\}_{\varphi_A^0}\eta^2 + \frac{1}{2}H(\nabla\eta)^2\right], \qquad (23)$$

where F_m is the free energy of mixing for a homogeneous solution. It is seen that Eqns.(2) and (23) for the free energy of mixing are almost identical.

Van Aartsen applied the Debye relations to systems based on high-molecular-weight components.[23] He began with the assumption that the Flory–Huggins expression is valid for ΔF_m in the case of a homogeneous solution:[24]

$$\frac{\Delta F_m}{V} = RT\left[\frac{\varphi_A}{\bar{V}_A}\ln\varphi_A + \frac{1-\varphi_A}{\bar{V}_B}\ln(1-\varphi_A) + \frac{\chi}{\bar{V}_A}\varphi_A(1-\varphi_A)\right], \qquad (24)$$

where $\bar{V}_A$ and $\bar{V}_B$ are the molar volumes of the solvent and the polymer respectively.

In this case one can write for the second derivative of the free energy with respect to composition

$$\left\{\frac{\partial^2(\Delta F_m/V)}{\partial\varphi_A^2}\right\}_{\varphi_A^0} = \left[\frac{1}{\bar{V}\varphi_A^0} + \frac{1}{\bar{V}_B(1-\varphi_A^0)} - \frac{2\chi}{\bar{V}_A}\right] \qquad (25)$$

If the relation

$$\chi = A + (B\bar{V}_A/RT) \qquad (26)$$

is valid for the Flory–Huggins parameter χ, Eqn.(25) can be transformed into

$$\left\{\frac{\partial^2(\Delta F_m/V)}{\partial \varphi_A^2}\right\}_{\varphi_A^0} = \frac{2RT}{\bar{V}_A}(\chi_{T_s} - \chi_T) = 2B\left(\frac{T - T_s}{T_s}\right), \qquad (27)$$

where χ_{T_S} is the interaction parameter corresponding to the temperature of the spinodal. It follows from the relations presented that the expression

$$\lambda_m = 2\pi l\,[3(1 - T/T_s)]^{-1/2} \qquad (28)$$

can be written for the optimum wavelength of spinodal decomposition.

Thus the most "critical" parameter for the determination of the dimensional characteristics of the microregions of phase separation in the given instance is the characteristic distance for the interaction of the molecules. Debye assumed that

$$l = 0.5\text{–}2 \text{ nm} \qquad (29)$$

for low-molecular-weight components and

$$l = R/\sqrt{6} \qquad (30)$$

for polymer–solvent systems. Here R^2 is the mean square of the distance between the ends of the polymer chain. For polymer–polymer systems, McMaster[25] suggested that l be determined from the relation

$$l = R/\sqrt{3} \quad . \qquad (31)$$

The most complete treatment of the phenomenon of spinodal decomposition in systems based on two high-molecular-weight components has been carried out in the theoretical studies of de Gennes[26] and Pincus.[27] An extension of the corresponding Flory–Huggins expression for an inhomogeneous system[28] was used in the above studies to formulate the free energy of the system:

$$\frac{F}{k_BT} = \frac{\varphi_A}{N_A}\ln\varphi_A + \frac{(1-\varphi_A)}{N_B}\ln(1-\varphi_A) + \frac{a^2}{36\varphi_A(1-\varphi_A)}(\nabla\varphi_A)^2, \qquad (32)$$

where a is the size of the monomeric unit and N_A and N_B are the degrees of polymerisation of components A and B respectively.

In the de Gennes theory account is taken of the fact that the main mechanism of the movement of molecular chains in polmer–polymer systems involves their reputation or "creep" in a tube formed by the labile nodes of the entanglement network.[29–31]

The time variation of the local composition of the system ϕ_A is related to the flux J_A of component A by the continuity equation

$$\partial\varphi_A/\partial t + \operatorname{div} J_A = 0 \quad . \qquad (33)$$

The Fourier component of the flux for the wave vector J_A is determined on the basis of the corresponding Fourier component of the chemical potential gradient of the given component $\nabla\mu(q)$ by means of the relation

$$J_A(q) = -[\Lambda(q)/k_BT](\nabla\mu(q)), \qquad (34)$$

where $\Lambda(q)$ is the Onsager coefficient. Having found $\nabla\mu$ and leaving in the expression for this quantity only terms linear in $\delta\phi(r)$, we have

$$\frac{\nabla\mu}{k_BT} = \nabla(\delta\varphi_A)\left(\frac{1}{N\varphi_A(1-\varphi_A)} - 2\chi\right) - \frac{a^2}{36\varphi_A(1-\varphi_A)}\nabla^3(\delta\varphi_A) \quad . \qquad (35)$$

Eqns.(33)–(35) have been used to obtain the so-called central relaxation formula:

$$\frac{1}{\tau_q} \equiv \frac{1}{\delta\varphi_q}\frac{\partial(\delta\varphi_q)}{\partial t} = q^2\Lambda(q)\left(\frac{1}{N\varphi_A(1-\varphi_A)} - 2\chi + \frac{a^2q^2}{36\varphi_A(1-\varphi_A)}\right). \qquad (36)$$

The relaxation spectrum, found on the basis of Eqn.(36), defines the initial unstable mode in the binary system and the rate of growth of this mode. Assuming a unique relaxation time for the mode of the wave vector q in a melt of two polymers, the Onsager coefficient obtained by de Gennes assumes the following form:

$$\Lambda(q) \simeq \varphi_A(1-\varphi_A)N_eD_1(qa)^2, \qquad (37)$$

where N_e is the number of monomeric units between the sites where the chains are hooked to one another and D_1 is the coefficient of microscopic diffusion. It follows from Eqn.(37) that the Onsager coefficient is proportional to the square of the wave vector, i.e. increases sharply with decrease of wavelength.

Subject to the condition $\chi \gg \chi_{T_1}$, i.e. after the instantaneous transfer of the system to a region lying within the spinodal on the phase diagram, we have from the central relaxation formula

$$-1/\tau_q = \chi\Lambda(q)q^2(2 - q^2l^2) \qquad (38)$$

where $l = 1/3a\chi^{-1/2}$ is the thickness of the interfacial transitional layer determined on the basis of the Helfand theory for polymer–polymer mixtures.[32,33]

Eqn.(38) shows that, when $ql < \sqrt{2}$, the composition fluctuations are enhanced, i.e. the system passes to the regime of spinodal decomposition. The greatest enhancement is characteristic of the optimum wavelength corresponding to the following wave vector:

$$q_m = 2\sqrt{3}a^{-1}\chi^{1/2} \quad . \qquad (39)$$

It is seen from Eqn.(39) that the optimum wavelength of spinodal decomposition is slightly smaller than the mean square radius of the molecular coil. In principle, this conclusion is inconsistent with the theoretical predictions based on the Debye–van Aartsen theory.

When account is taken of Eqn.(39), the rate of relaxation to the equilibrium two-phase state for the optimum wavelength is defined by the relation

$$-1/\tau_q = D_1N_e\chi a^2l^{-4} \equiv (N_e/\tau_1)\chi^3, \qquad (40)$$

where τ_1 is the time of the microscopic diffusion of a chain segment.

On the basis of the de Gennes central relaxation formula, Pincus[27] amended de Gennes' conclusion concerning the magnitude of the optimum wavelengths of spinodal decomposition. In particular, Pincus took into account the fact that, for the wave vector of non-interacting chains in the melt, there is not one but at least two independent relaxation modes.[34] As a result, we have for the Onsager coefficient when $qR_0 \gg 1$

$$\Lambda(q) = 2T\mu_1(ql)^{-2}[1 - \exp(-q^2R_0^2/6)]\varphi_A(1-\varphi_A), \qquad (41)$$

where μ_1 is the mobility of the monomeric unit.

Thus the Onsager coefficient proves to be proportional to the reciprocal of the square of the wave vector. On combining Eqns.(36) and (41), we obtain the following expression for the rate of relaxation of the system to the state of equilibrium:

$$\frac{1}{\tau_q} = \frac{1}{2}(T\mu_1/L^2)[1 - \exp(-q^2R_0^2/6)][N^{-1} + 2\chi\varphi_A(1-\varphi_A) + (qa)^2/36], \qquad (42)$$

where L is the contour length of the macromolecule. When $\tau_q < 0$, an exponential growth of the intensity of composition fluctuations is observed. The sharp transition from $\chi < 0$

to $\chi > \chi_{T_S}$ corresponds to the fact that the initial unstable mode q_m is specified by the extremum in Eqn.(42), i.e.

$$q_m^{-1} \simeq (R_0/6)\,[\ln(6\chi/\chi_{T_S})]^{-1},\quad \chi > \chi_{T_S} \qquad (43)$$

when the system passes rapidly from the one-phase state for into the region bounded by the spinodal. In the unstable region of the phase diagram near the spinodal, we have

$$q_m^{-1} \simeq (R_0/6\sqrt{3})\,(\chi/\chi_{T_S} - 1)^{-1/2},\quad (\chi - \chi_{T_S})/\chi_{T_S} \ll 1\ . \qquad (44)$$

For the optimum rate of growth of fluctuations in the former case, we obtain

$$1/\tau_{q_m} \simeq T_{rep}^{-1}(\chi/\chi_{T_S}),\quad \chi \gg \chi_{T_S}\ . \qquad (45)$$

In the second case we have correspondingly

$$\frac{1}{\tau_{q_m}} \simeq T_{rep}^{-1}\,(\chi/\chi_{T_S} - 1),\quad (\chi - \chi_{T_S})/\chi_{T_S} \ll 1\ , \qquad (46)$$

where T_{rep} is the time required for the molecular chain to emerge from the entanglements tube.

We shall note the most important features of Pincus' study, which constitutes a further development of the ideas of de Gennes.

1. The unstable mode has a wavelength comparable to the radius of the molecular coil and hence varies in proportion to $N^{1/2}$.

2. The rate of increase of the intensity of the composition fluctuations corresponding to the given mode is proportional to the reputation diffusion constant in the melt, varies as N^{-2}, and its concentration dependence is represented by a curve having the same form as the spinodal.

Thus Pincus' analysis of the phenomenon of spinodal composition in mixtures of homopolymers shows that microphase separation on the scale of distances of the order of magnitude of N_e is possible only for very intense cooling of the one-phase mixture of polymers. This case has been considered by de Gennes[35] in relation to cross-linked polymer blends. Quenching of this extent is equivalent to the fulfilment of the condition $\chi/\chi_{T_S} \gg N/N_e$. This is unlikely in blends of homopolymers under real experimental conditions. It is seen from the foregoing that, in the entire set of multicomponent polymer systems, only polymer–solvent and homopolymer–homopolymer systems have so far been analysed as regards spinodal decomposition in the region of unstable states on the phase diagram; more complex systems have been scarcely considered.

IV. EXPERIMENTAL STUDIES OF SPINODAL DECOMPOSITION IN SYSTEMS BASED ON HIGH-MOLECULAR-WEIGHT COMPONENTS

In the first study of the phase separation of polymer systems in the region of an unstable state, the poly-2,6-dimethyl-1,4-phenyl ether (PDMPE)–caprolactam system was investigated.[36] By measuring the scattered light intensity, it was established that cooling drives the solution to the region of unstable states on the phase diagram and phase separation then occurs via the spinodal decomposition mechanism. Microscopic observations on the phase separation processes have been made in the same system[37] and it was found that the size of the microdrops of the phase enriched in the polymer increases with time.

Phase separation in the PDMPE–toluene system has also been studied,[38] the increase in turbidity being recorded visually, while in another investigation[39] the same system was studied by electron microscopy. In those cases where homogeneous PDMPE–toluene mixtures were cooled to a temperature below T_S, two characteristic phenomena were observed. At a quenching temperature differing only slightly from the spinodal temperature, there is sufficient time for the formation of many nuclei in the system during the passage through the metastable region of the phase diagram. Cooling to a temperature somewhere above T_S gives rise to a pattern typical for phase separation via the nucleation and growth mechanism. On the other hand, if the system is cooled to a temperature somewhat lower than T_S, the electron microscopic patterns reveal the formation of two interlinked structures (structural networks) together with the nuclei.

Thus the rate at which the system passes through the metastable region on the phase diagram determines to a large extent the structure of the liquid mixture. On the other hand, if the homogeneous solutions are cooled to temperatures appreciably lower than T_S, the system passes rapidly through the metastable region and the electron micrographs show mainly interlinked structures characteristic of phase separation via the spinodal mechanism.

Phase separation in the polystyrene–decalin system has been investigated[40] and the dimensions of the regions corresponding to phase separation via the spinodal mechanism have been determined from light scattering data using the fundamental relations of Cahn's theory. The phenomenon of spinodal decomposition also proved to be typical for certain polymeric gels. Thus a diffraction maximum has been observed on the light scattering intensity curves for hydrogels and agarose, which is associated with the formation of regularly arranged phase separation regions.[41] A detailed investigation of phase separation in the sol–gel transition in the given system, occurring when it is cooled, was subsequently carried out.[42]

In conformity with Cahn's theory, in the majority of the studies considered the fulfilment of all the main criteria for the occurrence of spinodal decomposition mentioned above was assessed. It was shown that the occurrence of spinodal decomposition depends in many respects on the rate of transition of the system to an unstable state and, for solutions, also on the concentration, since in highly dilute systems the formation of modulated structures is altogether difficult.[9] In many instances the criteria of spinodal decomposition in solutions at a concentration above the critical value are fulfilled only in the initial stages of phase separation. In later stages nucleation apparently occurs.

A detailed study has been made[43] of phase separation in solutions of gel-forming atactic and isotactic polystyrenes, poly(phenylene oxide) and their mixtures in various solvents.[43] It was observed that the formation of a gel is not associated with crystallisation but is due to the transition of the system to the region of an unstable state on the phase diagram and the formation (as a result of fine dispersion) of microregions enriched in the polymer, the glass points of which are sufficient for the fixation of the ends of various polymer chains in a single vitrified region. The small size of the microregions (approximately 1000 Å) and the high rate of their formation are considered as evidence for the spinodal mechanism of phase separation of the liquid–liquid type. Fusion of the gel is attributed to the fact that, when the microregions are devitrified, the sections of the polymer chains bound by them are liberated. McMaster[25,44] investigated the system comprising the styrene–acrylonitrile copolymer and poly(methyl methacrylate). This system is characterised by a phase diagram with a lower consolute temperature. The interaction parameter can be represented as the sum of the enthalpy and entropy contributions, i.e.

$$\chi = \chi_h + \chi_s \qquad (47)$$

(χ_h and χ_s are the enthalpy and entropy components of the interaction parameter) and Eqn.(27) can be written as follows:

$$\frac{\partial^2 f}{\partial c^2} = \frac{2R\chi_h}{V_1}\left(\frac{T-T_s}{T_s}\right) . \quad (48)$$

The expression for k can be formulated thus:

$$k = \left(\frac{RT\chi}{V_1}\right) l^2/6 . \quad (49)$$

In this case the optimum wavelength of the spinodal decomposition is given by the relation

$$\lambda_m = 2\pi l \left(\frac{3\chi_h}{\chi T} \cdot \frac{T_s - T}{T_s}\right)^{-1/2} . \quad (50)$$

Thus, by neglecting the entropy contribution to the interaction parameter, it is possible to obtain Eqn.(28).[23] The development of phase separation microregions in time has been observed experimentally by transmission electron microscopy.[43] It is significant that, with increase of the heat treatment time, there was a gradual increase of the content of one of the components in the developing microregions. The diffuse interfacial layers then gradually became sharper and it was actually possible to observe the early stages of the coalescence of the microregions. The size of the microregions in the given stages of phase separation is approximately 50–100 nm. The interlinking of various microregions is characteristic of the early stages of the decomposition. For a composition remote from the critical composition, a very slow coalescence process, controlled by the Ostwald ripening mechanism, takes place after the attainment of equilibrium phase compositions.[45] Accordingly, the increase of the volume of the microregions of the disperse phase as a function of time is expressed by the relation

$$d^3 = d_0^3 + 64\tau (x_c V_m) Dt/9RT , \quad (51)$$

where d_0 is the diameter of the microregions after they have attained the composition of the equilibrium phases, x_c the mole fraction of the component entering into the composition of the disperse phase, V_m the molar volume of the given component, τ the disperse phase–matrix interfacial tension, and D the diffusion coefficient for the matrix phase. Using Eqn.(51), McMaster estimated the diffusion coefficient, which proved to be 9×10^{-16} m^2 s^{-1} for 538 K.

The data obtained for the phase separation of mixtures having the critical composition show that a relation of type (1) is applicable only to the description of the earliest stages of decomposition. In particular, as a result of heat treatment at 453 K, it is possible to observe in the course of only 4.4 min the simultaneous increase of the difference between the compositions of the microregions and the size of the latter. Thus, the use of the non-linear version of the Cahn–Hilliard relation of type (14) is now necessary for the description of the kinetics of phase separation.

McMaster[44] estimated the diffusion coefficient in mixtures having the critical composition by means of the relation

$$R(\lambda_m) = \left(-\Omega \frac{\partial^2 f}{\partial c^2}\right) \frac{2\pi^3}{\lambda_m^2} , \quad (52)$$

which follows from the Cahn–Hilliard theory. Accordingly it was found that the diffusion coefficients at 453 and 483 K are 2.6×10^{-18} and 3.3×10^{-17} m^2 s^{-1} respectively.

Thus McMaster was able to explain on the basis of the Cahn–Hilliard theory the most characteristic features of the early stages of the spinodal decomposition of a polymer–polymer system. He predicted correctly the scale level of the separation, which proved to be greater than in systems based on low-molecular-weight components.

In particular, the experimental determination of the diffusion coefficients in the early stages of the decomposition of a system having the critical composition and in the Ostwald ripening of the disperse phase in a system whose composition is remote from the critical composition must be recognised as specially important. A virtually new feature of the interpretation of the phase separation phenomena in polymer systems involves the explanation of the increased rate of growth of the phase separation microregions owing to coalescence due to the viscous flow of the components in "channels" formed by the interlinked structures. The appropriate analysis based on the use of a modified form of the relations for the stability of anisodiametric inclusions[46] yields a satisfactory agreement with experiment.

Nishi et al.[47] investigated the phase separation in the polystyrene (PS)–poly(methyl vinyl ether) (PMVE) system by NMR, light transmission, and optical microscopic methods. This system is also characterised by the presence of a lower consolute temperature. On the basis of morphological observations, the authors noted two types of phase separation in the systems investigated. Phase separation either proceeds at a high rate, giving rise to a characteristic network of interlinked microregions of approximately identical size, or, during slow phase separation, the microregions are spherical in shape from the very beginning. In the former case the microphase structure becomes finer as the temperature increases and in the last stage of the phase separation the microregions grow rapidly, remaining interlinked, and then either break up into small spheres or merge into macrospheres. In the latter case the dimensions of the microregions are small compared with the periods of interlinked structures.

Data obtained by pulse NMR confirmed the continuous variation of the composition of the microregions with time, which agrees with the hypothesis of the spinodal mechanism of the phase separation. Another piece of evidence for the spinodal mechanism is provided by the estimate of the quantity $R(q_m)$ in the Cahn–Hilliard equations, according to which the kinetics of the variation of the composition of the phase separation microregions can be described by the relation

$$c - c_0 = A(q_m) \exp[R(q_m)t] \cos q_m x \quad (53)$$

when

$$R(q_m) = \frac{1}{2} q_m^2 D \quad (54)$$

In the present case the quantity c represents the concentration of PMVE in the phase enriched in polystyrene. On this basis, it follows from Eqn.(53) that the total decrease of Q (of the content of PMVE) in the given phase during phase separation is described by the expression

$$Q = \left[\int_{\pi/2q_m}^{3\pi/2q_m} (c - c_0)\, dx\right]^3 = \left[\frac{2}{q_m} A(q_m)\right]^3 \exp(3R(q_m)t) . \quad (55)$$

We have the following time variation of $\ln Q$:

$$\ln Q = 3 \ln\left[\frac{2}{q_m} A(q_m)\right] + 3R(q_m)\, t \quad (56)$$

whose slope is $3R(q_m)$. The quantity $\ln Q$ is estimated from NMR data. The positive value of $R(q)$ shows that the concentration fluctuations become more intense with time, i.e. in the system containing 50% PMVE at 403 K spinodal decomposition takes place. If q_m is estimated from morphological data, we have for the diffusion coefficient

$$D = -2R(q_m)/q_m^2 = -2.8 \cdot 10^{-17} \text{ m}^2 \text{ s}^{-1} \quad (57)$$

when

$$R(q_m) = 3.82 \cdot 10^{-4}\ \text{c}^{-1};\ q_m = 5.24 \cdot 10^{6}\ \text{m}^{-1}. \quad (58)$$

A negative value of D indicates active transport in the system which is in the region of unstable states on the phase diagram.

The quantity χ, found on the basis of the Debye–van Aartsen theory, is −0.42 at 373 K, $k = 37 \times 10^{-13}$ J m^{-2} (in 1 m^3 of PMVE), and $f'' = -4.1 \times 10^6$ (in 1 m^3 of PMVE). The temperature of the spinodal for the given composition is 391 K and $l \cong 58$ nm.

Thus, on the basis of rigorous quantitative data, the spinodal mechanism of the phase separation in the PS–PMVE system has been demonstrated[47] and the principal characteristics of the phase separation process have been determined. As in the study of the phase separation in the system comprising the styrene–acrylonitrile copolymer and poly(methyl methacrylate) examined above, the periodicity of the modulated structure is much greater than in systems based on low-molecular-weight components. In particular the value of $\langle R^2 \rangle^{1/2}$ found by Nishi et al.[47] is very close to the radius of an unperturbed Gaussian coil. This is in full agreement with the de Gennes–Pincus theory.

The influence of particular factors, which determine the characteristic features of spinodal decomposition, has been examined in a number of studies. In particular, a study[48] has been devoted to phase separation in thin films of the PS–PMVE system. The authors showed that the conditions for spinodal decomposition then depend on the chemical nature of the support and on the thickness of the film. The influence of vitrification and of the presence of a low-molecular-weight component on the phase separation processes in the poly(phenylene oxide)–(*p*-chlorostyrene–*o*-chlorostyrene) copolymer system has been investigated.[49] A very sophisticated low angle technique for the investigation of the X-ray emission spectrum, involving the application of a position-sensitive detector, was used.

V. CHARACTERISTIC FEATURES OF PHASE SEPARATION IN BLOCK SYSTEMS

The results of a large number of theoretical[50–54] and experimental[55–60] studies show that phase separation is observed under certain conditions in high-molecular-weight compounds whose molecular chains consist of an alternation of blocks of different nature. As a result, microregions with equilibrium composition, whose size and shape depend on the "architecture" of the molecular chains and on the volume fraction of each block, are segregated. Since block polymers can be usefully treated as multicomponent polymer systems as regards phase separation, the same conditions for phase separation (based on the existence of binodals and spinodals) are valid for them as for the systems based on chains of different types not linked chemically. At the same time the results of theoretical and experimental studies have shown that the appearance of differences from traditional multicomponent systems is to be expected for polymeric materials of this kind. It must be assumed that such differences are capable of influencing significantly the phase separation processes and the final structure of multiphase systems.

Evidently, in those cases where the block copolymer relaxes fairly slowly from the spatially homogeneous state, the formation of a microphase structure can take place via the spinodal decomposition mechanism. This problem was considered for the first time with adequate rigour in two investigations[59,60], where it was shown that, whereas the condition for instability in homopolymer blends is considered only as regards instability with respect to separation into infinite homogeneous phases (with a wavenumber $q = 0$), for block copolymers it is considered as regards instability with respect to separation into microphases with a characteristic period of spatial inhomogeneity defined by the wavenumber $q = q_0 \neq 0$.

In the region of stability of a spatially homogeneous state, any small inhomogeneity decays exponeitially with a characteristic relaxation time. As the spinodal is approached, the relaxation times increase and on the spinodal become infinite. In the region of unstable states the amplitude of the inhomogeneities to which correspond negative eigenvalues of the matrix G_q^{-1} (the inverse matrix of the pair correlation functions in q-space) increases exponentially, resulting in the breakdown of the spatially inhomogeneous state. The periodic inhomogeneities with wavenumbers in the specific range $q_1 < q < q_2$ then grow, while the fluctuations with $q < q_1$ and $q > q_2$ again dissipate. After a time, the above range of wavenumbers becomes narrower until the formation of a heterogeneous structure with a characteristic period d_0 and the amplitude of the inhomogeneity increases exponentially. For "highly blended" heteropolymers, the period of the heterogeneous structure is of the order of magnitude of the correlation radius in the system of ruptured units. An increase of the average length of the chemically homogeneous sections results in an increase of the equilibrium values of the periodicity.

In connection with the characteristic features of the equilibrium microwave structure of block polymers, an interesting analogy, observed, on the one hand, in the behaviour of the block copolymers and, on the other hand, in that of multicomponent systems which decompose in the region of unstable states of the phase diagram, merits mention.[61] The point is that the transition from a one-phase solution of the blocks to the state of microphase separation is observed for block copolymers of the styrene–butadiene and styrene–butadiene–styrene systems as the temperature is reduced. A higher degree of microphase separation corresponded to a lower temperature. This was manifested by a gradual increase of the intensity of the low-angle X-ray scattering maxima with decrease of temperature. As shown previously, such phenomena characterise the spinodal decomposition of binary systems.[15] The analogy in the changes in the low-angle scattering curves proved extremely close; together with the characteristic increase of the intensity of the maxima, a decrease of the intensity in the "tail" section of the scattering curve and the presence of a common point of intersection of all the curves (cross-over) have been observed. Taking this factor into account, by analogy with Eqn.(18), Roe et al.[61] proposed the following expression for the intensity of the low-angle scattering in block systems in a state of equilibrium at different temperatures:

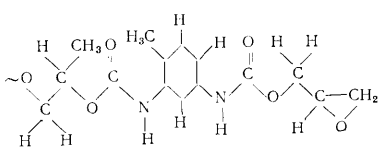
$$I(q, \chi) = I(q, 0) \exp(\alpha(q)\chi)\ . \quad (59)$$

Here the multiplier $\alpha(q)$ corresponds to the amplification factor used to describe the spinodal decomposition process and it is assumed that the thermodynamic interaction parameter varies with temperature in accordance with Eqn.(26). The multiplier $\alpha(q)$ has a maximum at $q = q_m$ and is zero at $q = q_c$. The ratio q_c/q_m is close to 1.5 (in the case of spinodal decomposition $q_c/q_m = \sqrt{2}$).

The temperature variation of the logarithm of the intensity of the low-angle scattering for two- and three-block copolymers of the type investigated is linear. This makes the analogy with the changes in the intensity of the low-angle scattering in spinodal decomposition quite unambiguous.

It seems natural to examine the question whether this analogy in the behaviour of block copolymers in equilibrium at different temperatures and blends in significantly non-equilibrium states in the course of spinodal decomposition is fortuitous. It is known that the increase of the period of the inhomogeneous distribution of the components in spinodal decomposition is limited by the finite rate of their diffusion. The latter is determined by the multiplier Dq^2 in Eqn.(11). The possibility of a decrease in the wavelength of the spinodal decomposition is limited by the increase of the free energy of the system [the term $2kq^2$ in Eqn.(11)]. An expression analogous to Eqn.(11), which determines the stability of the periodic microphase structure of systems of the same kind, is also valid for block copolymers at different temperatures. Taking into account the above analogy with the phenomenon of spinodal decomposition, in the case of block copolymers a multiplier similar to Dq^2 should reflect the fact that the microregions based on blocks of any kind are limited in size from below by the size of the corresponding molecular coils. Since the shape of the latter can be represented by the diffusion equation, it is quite possible that the geometrical effect indicated is associated with a multiplier proportional to q^2. On the other hand, the multiplier $f'' - 2kq^2$, which determines the increase of the size of the phase separation microregions, usually occurs in the thermodynamics of inhomogeneous liquid mixtures[8] and is therefore applicable to the description of block copolymers.

It is noteworthy that the phenomena examined above, associated with the microphase separation in block copolymers, have been observed[61] in relation to two- and three-block copolymers with a comparatively high molecular weight. It is all the more interesting that we observed a similar temperature variation of the intensity of the low-angle X-ray scattering for oligomers consisting of a single flexible small block (a butadiene–isoprene copolymer with a molecular weight of 4500) and two quite small terminal rigid blocks,[89]



each of which has a molecular weight of approximately 300. At 433 K this oligomer is characterised by such a weak level of low-angle scattering that it can be regarded as "transparent" in the X-ray emission spectrum. With decrease of temperature, the intensity of the low-angle scattering increases and a distinct maximum (Bragg period 8.3 nm) gradually appears on the intensity curve. In the temperature range up to 293 K its positions remains unaltered.

Thus, when the temperature is varied from 433 to 293 K, a microphase structure is formed in the given oligomer. It follows from the results obtained that the degree of enrichment of the phase separation microregions in a particular component increases under these conditions. This shows that a phase diagram with an upper consolute temperature is characteristic of a block copolymer treated as a binary system. Analysis of the dependence of the logarithm of the scattering intensity on the reciprocal of temperature shows that it is linear. Thus, on the basis of the characteristic features of the low-angle scattering curve and the validity of the Eqn.(59), one may conclude that the temperature variation of the changes in the microphase structure of the given oligomer is analogous, as in the study of Roe et al.,[61] to the structural changes observed in spinodal decomposition.

VI. PHASE TRANSFORMATIONS IN MULTICOMPONENT POLYMER SYSTEMS OCCURRING AS A RESULT OF CHEMICAL REACTIONS

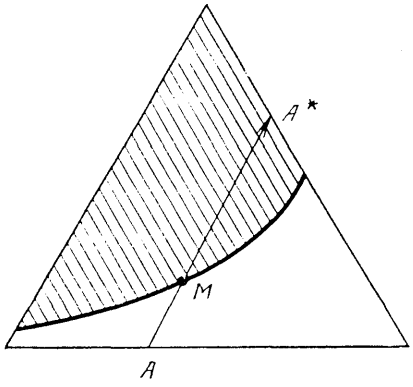
The systems examined above by no means exhaust all the versions of polymer systems potentially capable of undergoing phase separation in the region of unstable states on the phase diagram. It is known that phase separation can occur for reasons other than a change in temperature, pressure, or composition. There is an extremely wide range of systems (particular for high-molecular-weight compounds) for which phase separation is induced by chemical processes: degradation, polymerisation, depolymerisation, etc. In this case the systems can be of the simplest type (the monomer–polymer type) or can be very complex (for example, interpenetrating polymer networks based on several network polymers). The cases where the partial polymerisation of the monomer leads to the phase separation of the system into microregions enriched in the polymer and monomer are particularly widely known. The same is possible also in the partial depolymerisation of a macromolecular polymer.

The phase separation processes occurring on formation of carbon fibres as a result of the high-temperature treatment of polyacrylonitrile or cellulose hydrate fibres (carbonisation or graphitisation) are extremely characteristic and of practical importance.[62] This is known to entail the formation of a microporous structure characteristic of hydrocarbons with a pore size of the order of several nanometers.[63–66] The volume fraction of such micropores can reach 10%. Thus, as a result of carbonisation (heat treatment at approximately 1300 K) or graphitisation (heat treatment at approximately 2300–2800 K), a comparatively homogeneous polymeric material is converted into a heterogeneous carbon–micropores system. This can be explained by the fact that, in the course of the high-temperature treatment, the polymer is converted by chemical reactions into a carbonaceous material and gaseous product dissolved in the latter. At a specific stage of the transformations, phase separation takes place with segregation of liquid and gaseous phases, the latter forming the micropores. The very small sizes of the micropores and their comparatively narrow distribution can be regarded as a consequence of the fact that phase separation takes place via the spinodal decomposition mechanism and not via nucleation and growth.

The phase separation processes in the formation of a network polymer in an oligomer–solvent system have been investigated in relation to the polymerisation of oligoacrylate esters. The initial system consisted of a solution of αω-dimethacrylatebis(diethylene glycol phthalate) in tetrahydrofuran or in its mixtures with toluene or hexane. The polymerisation was carried out via an anionic mechanism. It was shown that the polymerisation of the oligomer leads to a sharp increase of the intensity of the low-angle X-ray diffraction. The cause of such appearance of "turbidity" is microphase separation of the system at the level of approximately 1–100 nm. The characteristics of the microphase structure, estimated from structural data, proved to depend on the type of the low-molecular-weight solvent. This is manifested by the fact that the curves for the distribution of the microheterogeneous regions with respect to size are characterised by different widths.

Since the microheterogeneity thus produced is a result of phase separation in the oligomer–solvent–network polymer system, we shall consider a hypothetical phase diagram for such a system (see Figure). The shaded part of the diagram represents a two-phase region and the unshaded part a one-phase region. The sequence of states occurring in the

system during the polymerisation of the oligomer is indicated by the $A-A^*$ straight line. In the initial state the solution of the oligomer in the solvent constitutes a one-phase system. As the oligomer is consumed, the system intersects the binodal at point M and enters the region of two-phase states. It then tends to separate into phases enriched in the polymer and the solvent. Bearing in mind the traditionally small extent of the region of metastable states in systems based on high-molecular-weight components, one may expect that the nucleation processes play an insignificant role and, after a short time has elapsed following the transition through the binodal, the system enters the region of unstable states on the phase diagram where its separation takes place via the spinodal decomposition mechanism. This is confirmed by the small sizes of the phase separation microregions and their comparatively narrow distribution.



Phase diagram for a polymerising polymer–oligomer–solvent network system. Initial state (A): oligomer–solvent; final state (A^*): network polymer–solvent. During the polymerisation process, the system passes through a sequence of states corresponding to the AA^* straight line. The region of two-phase states is shaded.

Together with phase separation processes, a three-dimensional network of chemical bonds is formed in the system. The cross-linking establishes a definite inhomogeneity in the distribution of the components and hence hinders the further occurrence of the phase separation processes required for the attainment of the state of equilibrium. This leads to the formation, in a system undergoing polymerisation, of a non-equilibrium microphase structure which is a result of incomplete phase separation. For systems containing different solvents, the phase diagrams are characterised by different positions of the phase equilibrium curves. Accordingly the system begins to separate at different times, i.e. for different compositions. Consequently cross-linking leads to different instants of phase separation and different levels of heterogeneity.

The gel produced as a result of polymerisation is a system with alternation of microregions enriched in the network polymer or the solvent. The absence of interference maxima from the low-angle scattering curves shows that polymerisation results in the fixation not of the initial stages of the spinodal decomposition, characterised by a regular alternation of microregions, but of later stages in which this periodicity has already disappeared. The latter may be a consequence of the polydispersity of the microregions formed during later stages of decomposition owing to coalescence.

We believe that such treatment of the appearance of heterogeneity in network polymers formed in the presence of a solvent is more constructive and more general compared with the ideas concerning the appearance of heterogeneity owing to microsyneresis used for purposes of this kind.[67] In this connection it is noteworthy that the thermodynamics of chemical reactions is in essence the non-linear thermodynamics of irreversible processes. The appearance of heterogeneity in reacting systems is therefore the rule rather than the exception. In those cases where diffusion fluxes of the components in systems of this kind are directed along the concentration gradient, diffusion smooths out the local inhomogeneity induced by the occurrence of the reaction. However, if the system is in the region within the spinodal as a result of polymerisation, the diffusion fluxes change direction and do not lead to the smoothing out of the local inhomogeneities. Thus the heterogeneity observed in cross-linked gels can be explained as a result of the formation of dissipative structures (see below), which become fixed as a result of cross-linking.

The kinetics of phase separation in the formation of network block copolymers have been studied in relation to a system whose initial components are oligoisoprene dihydrazide with a molecular weight of 3100 and the diglycidyl ether of di(4-hydroxyphenyl)propane (DGEHP).[68] The system was hardened at a temperature above the point corresponding to the appearance of turbidity (at 383 K). Throughout the hardening process, the scattering of X-rays in the reaction mixture was recorded continuously. The system was initially completely "transparent", but, after a definite polymerisation time had elapsed, a gradual appearance of turbidity was observed. The angular dependence of the X-ray scattering intensity then showed an interference maximum whose magnitude increased with time.

Thus the blend of the initial oligomers is a one-phase system and the formation of a system of chemical bonds between them leads to microphase separation at the level of several nanometers. The time dependence of the logarithm of the scattering intensity in the initial stages of the polymerisation obtained from diffraction data is linear. This shows that in the initial stages of phase separation the rules governing spinodal decomposition are fulfilled in the case considered. This effect, which has not been observed hitherto in systems of the block copolymer type, permits the conclusion that the kinetics of the phase separation of block systems do not differ fundamentally (at least in the early stages) from those of the phase separation of the usual binary systems in the region of unstable states on the phase diagram and involving the spinodal decomposition mechanism.

Studies of the above network polymer over a wide range of temperature have shown that, in the range from 293 to 533 K, the state of microphase separation is maintained. However, the characteristic features of the diffraction patterns discussed in the previous section, which are characteristic of linear block polymers and oligomers, are not then observed. This fact probably indicates significant deviations of the microphase structure of the network polymer from the state of equilibrium at different temperatures. It is to be supposed that this deviation is determined to a large extent by the presence of a three-dimensional network of chemical bonds, which limits the mobility of blocks of different nature and leads to the appearance of non-equilibrium structures. As a result of this, the state of the system can no longer be described from the standpoint of equilibrium thermodynamics.

Microphase separation is a typical process, which occurs also in the formation of interpenetrating polymer networks (IPN).[69,70] In particular, this has been convincingly demonstrated for IPN based on polyurethane and the styrene–divinylbenzene copolymer. It follows from the low-angle scattering data obtained for the above system that the formation of the IPN leads to a significant alteration of the profile of the low-angle scattering curves. Consequently, the formation of microregions enriched in the matrix and penetrated by networks is characteristic of such IPN. Between the regions indicated, there are transitional zones with a smooth profile of the variation of concentration. This picture of the microphase structure indicates the formation of the IPN of "diffuse" microphase regions characteristic of the early stages of the spinodal decomposition. The absence of the interference maxima characteristic of the spinodal decomposition of the system from the low-angle scattering curves for the IPN considered shows that partial coalescence of the segregated microregions has taken place in the system, as a result of which the periodicity in their disposition has been significantly impaired.

Thus network polyblock polymers and IPN are characterised by the presence of stable "diffuse" phase separation microregions, i.e. the degree of segregation of the components in such microregions can be extremely remote from equilibrium values. This quantity is defined by the expression[71,72]

$$\alpha = \overline{\Delta\rho^2} \Big/ \overline{\Delta\rho_c^2} = \overline{\Delta\rho^2} \Big/ [\varphi(1-\varphi)(\rho_1-\rho_2)^2] \quad , \qquad (60)$$

where $\overline{\Delta\rho^2}$ is the average square of the electron density fluctuation calculated from the absolute low-angle scattering intensity, $\Delta\rho_c^2$ the theoretical estimate of the average square of the electron density fluctuation obtained on the assumption of microphase separation at the level of the pure components, ϕ the volume fraction of one of the components, and ρ_1 and ρ_2 are the electron densities of components A and B respectively. A detailed analysis of data on the relation between phase separation and the degree of segregation in various multicomponent systems undergoing phase separation has been carried out in a monograph.[72] We shall consider the question of the relation between two-phase systems and systems with a comparatively high but nevertheless remote from unity degree of segregation of the components.

Numerous experimental data[72] show that the degree of segregation of the system components in microphase separation depends on many factors: the presence or absence of transverse chemical bonds in the system, the cross-linking density, composition, etc. Evidently in the phase separation beginning after the system has passed from the one-phase state to the region of unstable states, the stable entanglement nodes prevent the separation of fragments of different chemical nature, as a consequence of which the system is held in a state of "enforced" blending. This should lead to an additional contribution to the free energy of the system.

Thus the situation is to some extent similar to the phenomenon of the stabilisation of metallic alloys within the region bounded by the limited chemical spinodal. However, for polymer systems, it is at present impossible to obtain an exact estimate of the contribution of the elastic energy arising under these conditions. Even for much simpler systems of the type of low-molecular-weight glasses, it has been shown[16] that the spinodal decomposition is complicated as a result of the possibility of the relaxation of stresses leading to a time variation of the elastic energy. In order to take it into account, the elastic energy at time t can be converted into the elastic energy at time $t + \Delta t$ in accordance with the equation

$$E_{rel}(t+\Delta t) = E_{unrel}(t)\exp(-2\Delta t/S), \qquad (61)$$

where $S = \nu_\nu \Theta M^0/\lambda^2 G_S$, ν_ν is the shear viscosity, G_S the modulus of shear, M^0 the mobility of the molecules, and Θ the thermal energy per molecule.

It is quite evident that the contribution of the elastic energy in complex multicomponent systems is minimal at the beginning of the phase separation process and should increase with increase of the difference between the compositions of the microregions. As a result, when the thermodynamic driving force of the phase separation is balanced by the contribution due to elastic stresses caused by the entanglements of fragments of the network structure, the system is stabilised in a state of partial separation of the components.

The limit of the stability of the stressed state of a polymer system is in this case characterised by the position of the curves located below the chemical spinodal. This curve reflects the real condition governing the transition to the two-phase state. We have called it the lower real spinodal. We note yet again the significant difference between the concept of the coherent spinodal introduced by Cahn and the concept of the real spinodal which we have resorted to in order to describe the limit of stability in the transition to the two-phase state of polymer systems.[73] The coherent spinodal is known[9,10] to be a curve outside which no processes involving the decomposition of the one-phase solution are possible. The real spinodal is a curve separating the state of partial phase separation from the two-phase state. It follows from Eqn.(17) that, for systems with an upper consolute temperature (UCT), the real spinodal passes below the corresponding chemical spinodal. It must be assumed that for certain systems, such as polyblock network polymers or interpenetrating polymer networks, the region of unstable states within the lower real spinodal lies far below the chemical spinodal and may be altogether inaccessible.

The results of temperature studies of the epoxydiene networks examined above have shown that systems of this kind can be not only in a state of enforced blending but also in a state of enforced microphase separation of the components. If the presence of a UCT is characteristic of systems of this kind, then completion of the transition to the state of a one-phase solution corresponds to a curve lying above the chemical spinodal. This curve can be called the upper real spinodal. Its position is determined by the elastic stresses, which are necessary, in the absence of free migration of blocks of different chemical nature, for the transition of the system with microphase separation to the one-phase state by heating.

Thus, depending on the previous history, multicomponent polymer systems with a three-dimensional network of chemical bonds can possess a more or less extensive region in the vicinity of the chemical spinodal in which states with partial phase separation of the components are realised. Evidently, in the transition from the one-phase state to the two-phase state, one-phase systems with an equilibrium distribution of composition fluctuations exist above the chemical spinodal. Below the real spinodal, there are two-phase systems with a definite degree of dispersion.

In the system between the chemical and real spinodals, there are also microregions with an inhomogeneous distribution of the components. However, they can no longer be regarded as equilibrium composition fluctuations, because thermodynamic forces, tending to cause phase separation, displace the system from the state of equilibrium towards an approach to the two-phase state. Despite the failure of the phase separation process to reach completion, the region of states between the chemical and real spinodals is relatively stable. However, in terms of the concept of "one-phase–two-phase system", within the framework of which we operate

in considering binary systems, there are no analogues of such intermediate states.

Systems of this kind can be usefully segregated from the set of one- and two-phase systems. The expression "concentration fluctuation" really has no bearing on the microregions (states) in the system located in the region of the phase diagram between the chemical and real spinodals, because it is applicable only to one-phase systems. Nor can they be called microphase regions, because the latter are characteristic only of two-phase systems. Bearing in mind that the microregions of inhomogeneity in systems intermediate between one- and two-phase systems are in principle capable of passing into microphase regions, they can be regarded as virtual microphase regions and can be referred to accordingly as phasons.[73] The system located in the region of states between the chemical and real spinodals is a system of the phason type.

We shall consider how such a system differs from the "classical systems" undergoing spinodal decomposition in the Cahn–Hilliard theory. According to the conditions in the phase separation mechanism, the term Y in Eqn.(17), which defines the limit of instability (i.e. the onset of spinodal decomposition), can be a function of time, temperature, the degree of segregation attained at the given instant, etc. After the system has reached the region of the chemical spinodal and, following the loss of stability, processes increasing the contribution of Y develop in it in the course of time, after which, following the attainment of a particular instant (as a consequence of relaxation processes or chemical reactions), they diminish this contribution. Therefore, having begun to decompose, the system can be additionally stabilised at some stage or the stabilisation effect vanishes completely. If this condition did not obtain, then, on transition through the chemical spinodal, the system would have undergone no changes whatever. This factor actually determines the appearance of phason systems, the main characteristic of which is the degree of separation into phases. Specific dimensions of the order of magnitude of tens of nanometers are characteristic of the corresponding microregions of heterogeneity.

VII. EXAMINATION OF SPINODAL DECOMPOSITION WITHIN THE FRAMEWORK OF THE FORMALISM OF THE NON-LINEAR THERMODYNAMICS OF IRREVERSIBLE PROCESSES

The conditions for thermodynamic equilibrium in isolated systems is an entropy maximum, while for systems at a fixed temperature it is a minimum in the Helmholtz free energy. When these requirements are taken into account, the corresponding systems can be described by equations whose solution corresponds to the so-called thermodynamic branch. If the action on the system is varied in such a way that the latter moves further and further away from equilibrium, non-equilibrium thermodynamics makes it possible to formulate an adequate condition for the stability of the thermodynamic branch.[74,75] On the other hand, if this condition is not fulfilled, then the thermodynamic branch can become unstable and the appearance of a new structure characterised by coherent behaviour will become possible in the system.

Thus a new type of organisation, linking the coherent space–time behaviour of the system to dynamic processes within it, can arise outside the region of stability of the thermodynamic branch. In the studies of Prigogine and co-workers,[74,75] it has been shown that the so-called dissipative structures appearing under these conditions differ significantly from the "equilibrium structure" studied by classical thermodynamics. An analogy has been noted,[76,78] between the alternation of low- and high-energy regions, characteristic of the dissipative structures, and the appearance of modulated structures as a result of spinodal decomposition. Having expressed the thermodynamic forces and fluxes in terms of concentration gradients, Prigogine showed that the following relation is valid for the increment in the generation of entropy near the stationary state of the system:

$$\Delta P = \int_V \left[\frac{1}{2} \delta^2 P + \sum_{kl}' R_{kl} \nabla c_k \nabla c_l + \ldots \right] , \qquad (62)$$

where

$$R_{kl} = D_{kl} \left(\frac{1}{T} \frac{\partial \mu_l}{\partial c_k} \right) .$$

For a binary system, the last term of Eqn.(62) is analogous to the term $k(\nabla c)^2$ in Eqn.(2) and $\frac{1}{2}(\partial^2 f/\partial c^2)(c - c_0)^2$ corresponds to $\frac{1}{2}\delta^2 P$ in the expansion of the increment of the generation of entropy. Thus the spinodal can be regarded as representing the condition for the equality of the excess generation of entropy to zero. Comparison of the above relations makes it possible to express the wavelengths of the modulated structure in spinodal decomposition in the following form

$$\lambda_m = \left[-8\pi (c - c_0)^2 \sum_{kl}' R_{kl} + \ldots \Big/ \sum_k \delta J_k \delta X_k \right] , \qquad (63)$$

where J_k and X_k are the generalised flux and force. Consequently the formation, as a result of phase separation, of diffuse microregions intermediate between the initial one-phase and the resulting two-phase systems can be regarded as a result of the breakdown of the stability of the phase separation process within the spinodal. The thermodynamic forces then tend to a minimum and the kinetic fluxes can increase in one part of the system and decrease in another, leading to the formation of dissipative structures.

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As already mentioned, the theory of spinodal decomposition was developed approximately 20 years ago by Cahn, Hilliard, Hillert and their successors to describe the processes occurring in metallic alloys. In the thermodynamics of polymers this period has been characterised by an intense development of a general theory of polymer solutions. During the last 20 years, much attention has been devoted to the application of the Flory–Huggins theory of solutions to the description of polymer blends and their thermodynamic compatibility has come to be regarded as one of the most important factors determining the operational properties of polymeric materials. Studies on spinodal decomposition in polymer system began to develop only in the last 10 years. We believe that this has been due to the increasing practical application of polymer blends, as shown, in particular, by the publication of a number of large monographs on these questions.[79–82]

The data which we have considered show that the spinodal mechanism of phase separation in polymer blends is the decisive factor in structure formation in such blends and hence in establishing the entire set of the physicomechanical properties of these materials. In the first place one should note polymeric composite materials and the clear tendency to employ in the latter second generation binders. Such binders may be either alloys and blends of thermoplastic polymers or systems of the type of interpenetrating, half-interpenetrating, and segregated networks,[83] which should

be regarded as hybrid binders.[88] A characteristic feature of second generation binders is that in essence they are themselves composite materials whose properties are determined to a large extent by their phase state and, as can be seen from the foregoing, by the character and the degree of completion of the phase separation in hybrid binders during their formation. An important task in the thermodynamics of polymer–polymer blends is therefore the accumulation of experimental data and the determination of the fundamental characteristics of the phase separation via the spinodal mechanism as a function of the parameters of the thermodynamic interactions of the components, the conditions in their polymerisation or polycondensation, the cooling regimes, and similar factors.

Only the main theoretical postulates have now been formulated and the applicability of the theory to the description of the experimental data has been demonstrated in relation to what are so far limited instances. The question of the relation between the phase separation conditions and the conditions for the interaction of binary polymer systems with fillers is important for the creation of composite materials based on second generation binders. Only a limited number of experimental data are so far available on this question.[84–87] At the same time one may claim that the introduction of a filler into the system can exert at least two different effects on the spinodal decomposition. If one of the components of the binary system interacts preferentially with the surface, the filler should promote an increase of the rate of phase separation. If the energies of the interaction of the components with the surface are approximately the same, then, as a consequence of the adsorption effects and the overall decrease of molecular mobility near the interface, phase separation processes may be inhibited. It can be shown that, under certain conditions, there is also a possibility of a change in the positions of the phase equilibrium curves (binodal and spinodal) under the influence of the surface of the solid.

The data presented in this review show that the structures arising as a result of spinodal decomposition in polymer–polymer systems then remain in a metastable state, i.e. as a rule the spinodal decomposition does not reach the stage where the system is fully separated into two coexisting phases. Otherwise studies on these lines would have been only of purely theoretical interest. However, it follows from this that evidently the most adequate description of the structures produced can be achieved using the principles of irreversible thermodynamics and the concept of dissipative structures. We believe that studies on polymer–polymer systems within the framework of the formalism of irreversible thermodynamics should have priority in the future over studies based on the apparatus of the classical thermodynamics of phase equilibria.

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Institute of the Chemistry of Macromolecular Compounds,
Academy of Sciences of the Ukrainian SSR,
Kiev

Translated from *Uspekhi Khimii*, 53, 1222-1246 (1984) U.D.C. 547.1'116:542.943

The Preparation of Monomers for the Synthesis of Fluorocarbon Polymers by the Oxidation of Fluoro-olefins

L.F.Sokolov, P.I.Valov, and S.V.Sokolov

The oxidation reactions of fluoro-olefins are examined: the conditions under which they take place, the characteristic features of the mechanism, and the composition and structure of the products formed. Attention is concentrated on the oxidation reactions of industrial perfluoro-olefins, namely tetrafluoro-ethylene and hexafluoropropene, and also on the methods of synthesis of the most important products of the oxidation of fluoro-olefins - fluorocarbonepoxides and oligomeric perfluoro-polyesters.
The characteristics of the physicochemical properties and the main applications of oxygen-containing products of the oxidation of fluoro-olefins are discussed.
The bibliography includes 154 references.

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I. INTRODUCTION

Fluorocarbon polymeric materials (plastics, elastomers, and lubricants) play an important role in the application of atomic energy, in machine construction, in chemical industry, and in other branches of the economy by virtue of their high chemical and thermal stability. The chemistry and technology of "second generation" fluoro-polymers, namely oxygen-containing polymers, is nowadays developing vigorously. The introduction of ethers and reactive functional groups into the main chain and into the side groups of fluorocarbon polymers makes it possible to extend significantly the temperature range of their use, while retaining a high chemical stability. A way of synthesising the monomers for oxygen-containing fluorocarbon polymers was discovered in the course of the study of the oxidation reactions of fluoro-olefins.

In contrast to saturated fluorocarbon compounds, which have a high chemical and thermal stability,[1,2] fluoro-olefins are readily oxidised at the double bond via both ionic and radical mechanisms and in this respect show similarity to hydrocarbon olefins. There is also a similarity in the chemical nature of the products of the oxidation of hydrocarbon and fluorine-containing olefins, but the mechanism of the oxidation of fluoro-olefins and the properties of the products have important characteristic features.

Among the products of the oxidation of fluoro-olefins, epoxides and oily products with a perfluoropolyether structure are of greatest practical interest.

Perfluoroepoxides were first obtained approximately 20 years ago by the oxidation of fluoro-olefins by a number of investigators simultaneously[3-9] and this approach to the synthesis of fluorocarbon epoxides still remains virtually the only one available.

The practical importance of fluorocarbon epoxides is indicated by the fact that the manufacture of the most important of these, namely epoxyhexafluoropropane (EHFP), was initiated in the USA in the middle 1960's.[10-12] The perfluoropolyether oils formed in the high-temperature photochemical oxidation of hexafluoropropene, are manufactured on an industrial scale under the trade name "Fomblin" in Italy and under the trade name "PEF" in the USSR.[13] A number of oxygen-containing fluorocarbon materials of practical importance have been obtained on the basis of the oxidation products of fluoro-olefins: solvents, surfactants, thermally and chemically stable fluororubbers with improved frost resistance,[14,15] perfluoropolyether oils and greases with exceptionally effective viscous-temperature characteristics,[13] fluorinated plastics with improved thermal stability,[16] perfluorinated ion-exchange membranes,[17-19] polymers with selective permeability to gases,[20] etc.

The great practical value of the above materials stimulated vigorous investigation of the oxidation reactions of fluoro-olefins. A number of reviews on the synthesis, properties, and applications of fluorocarbon epoxides[21-23] and oxygen-containing fluorocarbon polymers,[10,13,24] involving questions concerning the oxidation of fluoro-olefins, have been published in recent years, but there is no systematic review of the literature data on the oxidation of fluoro-olefins.

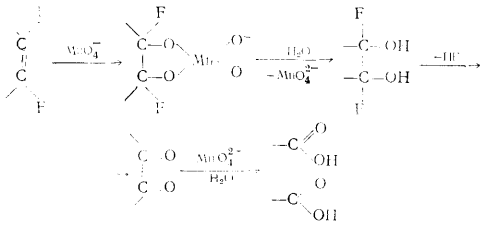
This review discusses what we believe to be some of the most significant questions of the mechanism of the oxidation of fluoro-olefins and the characteristics of the properties of their oxidation products. Attention has been concentrated on the oxidation reactions of two important industrial perfluorinated olefins, namely tetrafluoroethylene (TFE) and hexafluoropropene, with formation of the most important oxidation products—fluorocarbon epoxides.

II. IONIC OXIDATION REACTIONS OF FLUORO-OLEFINS

The oxidation of fluoro-olefins via the ionic mechanism proceeds under mild conditions (atmospheric pressure, room or reduced temperature) in the liquid phase in polar solvents; the oxidants are compounds containing active oxygen: hydrogen peroxide, metal hypohalites, potassium permanganate, etc.

The most important feature of the oxidation of fluoro-olefins via the ionic mechanism is preference for the nucleophilic mechanism due to the increased sensitivity of fluoro-olefins to nucleophilic attack.[25] The epoxidation of fluoro-olefins is accompanied by the simultaneous reaction

leading to the cleavage of the carbon skeleton at the olefin double bond. The first studies were devoted to oxidation processes with dissociation of the double bond and their results have been examined in a review.[25] The most important of these methods involves oxidation with potassium permanganate in neutral or basic aqueous and acetone media. A characteristic feature of such reactions is total hydrolysis of the C–F bonds involving the carbon atoms at the double bond undergoing the dissociation; this entails the formation of carbonyl-containing products: carboxylic acids, CO_2, and ketones:[25]



The hydrolysis of C–F bonds takes place as a consequence of the instability of the intermediate perfluorinated alcohols.[1] The partial conversion of the bound organic fluorine into an inorganic form is a serious technological disadvantage of ionic oxidation processes.

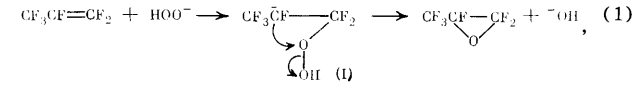
Fluoro-olefins are oxidised by hydrogen peroxide and metal hypohalites in an alkaline medium with preferential formation of epoxides accompanied by side reactions involving oxidation with dissociation of the double bond and also the total hydrolysis of the C–F bonds where the carbon atoms are also part of the double bond undergoing dissociation and the formation of carbonyl-containing products.

The process in which fluoro-olefins are oxidised by an alkaline solution of hydrogen peroxide, developed as early as 1967,[26] still remains one of the main procedures for the synthesis of fluorocarbon epoxides. The oxidation proceeds only in an alkaline medium and the nature of the alkaline agent has no significant influence on the process. KOH, NaOH, NH_4OH, etc. are usually employed. The reaction medium is water; below 273 K, a mixture of water with organic solvents such as methanol and ethanol is used to prevent freezing.[3,26–29] Fluoro-olefins are sparingly soluble in water and alcohol and the reaction therefore proceeds at the interface between the fluorocarbon and aqueous alcoholic phases. The pressure in the system has almost no effect on the oxidation reaction; the process is usually carried out at atmospheric pressure and temperatures between 223 and 323 K;[26] with increase of temperature, the yield of the epoxide diminishes owing to oxidation with rupture of the double bond and with decrease of temperature the rate of epoxidation is appreciably reduced.

An important feature of the method is its universality; it is suitable for the epoxidation of aliphatic fluorocarbon α-olefins,[3,26] internal and cyclic perfluoroalkenes,[30] incompletely fluorinated alkenes,[26] perfluorinated dienes,[31] etc. and the increase of the number of carbon atoms in the fluoro-olefins from 3 to 20 does not influence the rate of epoxidation.[26] However, epoxytetrafluoroethane (ETFE) cannot be obtained by this method.[3,10–12,30]

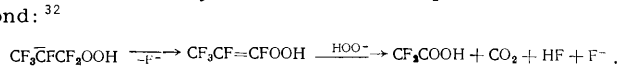
The oxidation with an alkaline solution of hydrogen peroxide is the first method of synthesis of a fluorocarbon epoxide applied on an industrial scale: the Dupont Corporation (USA) has manufactured EHFP since the middle 1960's by oxidising HFP with a 30% aqueous hydrogen peroxide in the presence of methanol and KOH at 243 K and pH of the medium above 8.[10] The yield of EHFP is then about 45%.[11,12] The EHFP obtained in this way contains only HFP and CO_2 as impurities.

The following epoxidation mechanism, incorporating a stage in which the hydroperoxide anion adds to the fluoro-olefin by a nucleophilic mechanism with subsequent elimination of a hydroxide anion, has been proposed:[10]

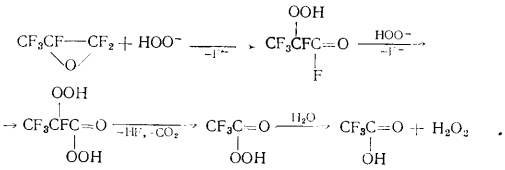


(1)

The intermediate anion (I) can also eliminate a fluoride ion, which leads ultimately to oxidation with rupture of the double bond:[32]



Under oxidation conditions, EHFP reacts relatively easily with the hydroperoxide anion to form acid products:[32]



The acid products formed neutralise the alkali which catalyses the oxidation. Because of this, the reaction is carried out with continuous supply of alkali to the solution in a far from catalytic amount.[33] When the addition of alkali is stopped, the process is rapidly arrested and the selectivity with respect to the oxide is reduced (Fig.1). The low selectivity (50–70%) even at a low conversion of the olefin (Fig.1) is striking. The selectivity in the epoxidation of other fluoro-olefins by hydrogen peroxide is within the same limits.[2,16]

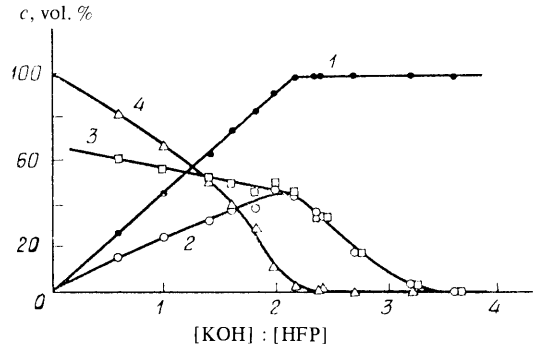


Figure 1. The influence of the molar ratio [KOH]:[HFP] on the composition of the products of the oxidation of HFP (c) with an alkaline aqueous-alcoholic solution of hydrogen peroxide at 273 K: 1) coversion of HFP; 2) yield of EHFP relative to the initial HFP; 3) yield of EHFP relative to the HFP which has reacted; 4) content of HFP in the oxidation products.[32]

A yield of the epoxide of the order of 50% is obtained also in another familiar process: the nucleophilic oxidation of fluoro-olefins by alkali and alkaline earth metal hypohalites in an aqueous alkaline medium in the presence of an aprotic

polar solvent (acetone, diglyme) at room temperature and atmospheric pressure.[34,35]

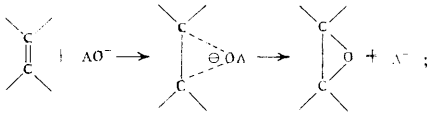
The low selectivity of the epoxidation in nucleophilic oxidation reactions of fluoro-olefins is due to the fairly high probability of the elimination of the fluoride ion from the intermediate anion (I) and the partial consumption of the epoxide in the reaction with the nucleophilic epoxidising agent.

For comparison, one may note that hydrocarbon olefins undergo epoxidation as a rule via an electrophilic mechanism and the oxidants are hydroperoxides and peracids and there is a quantitative (95–99%) yield of the epoxide and the C–H bonds are not involved.

Valuable information about the direction of attack on the double bond by the epoxidising agent and about the structure of the transition state is provided by data on the stereochemistry of the epoxidation reaction. The preferential formation of the epoxide and the stereospecificity of the epoxidation of hydrocarbon olefins by hydroperoxides and peracids are due to the specific direction of electrophilic attack on the bonding orbital of the double bond and the formation of an intermediate π-complex in the reaction[37] (see also Mathieu and Panico,[38] p.319).

The nucleophilic mechanism of the epoxidation of hydrocarbon olefins operates only in the oxidation of αβ-unsaturated carboxylic acids by alkaline hydrogen peroxide[39] and the reaction is non-stereospecific.[40,41] The latter is due to the specific direction of the nucelophilic attack on the antibonding π* orbital of the hydrocarbon olefin[38] (p.295) and the formation in the reaction of an intermediate carbanion of type (I) in which there is ready rotation about the C–C bond.[40,41]

In this connection, a report of the stereospecificity of the nucleophilic epoxidation of fluoro-olefins by hypohalites in an alkaline medium is of special interest:[34,36] since the double bond in fluoro-olefins is depleted in electron density[1] (pp.25, 30), this indicates nculeophilic attack on the bonding π orbital of the fluoro-olefin and the formation of an intermediate cyclic π-complex in the reaction:



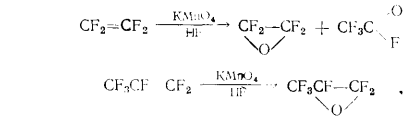
$AO^- = ClO^-$ BrO^- etc.

Thus, the fact that in the chemistry of fluoro-olefins electrophilic epoxidation via hydroperoxides and peracids has been replaced by reactions involving nucleophilic epoxidation by alkaline hydrogen peroxide and hypohalites via the opposite mechanism is a consequence of the radical alteration of the nature of the interaction of the double bond with the epoxidising agent on passing from olefins to fluoro-olefins. The mechanism of the attack on the double bond of the fluoro-olefin by the nucleophilic epoxidising agent is analogous to the mechanism of the attack on the double bond of a hydrocarbon olefin by the electrophilic epoxidising agent.

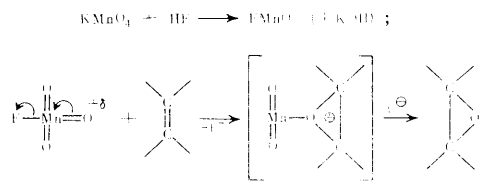
The reversal of the reaction mechanism in relation to the analogous reactions in organic chemistry is characteristic of fluorocarbons. For example, alkylation in the chemistry of hydrocarbon compounds is catalysed by acids,[38] while in the organofluorine chemistry it is catalysed by bases;[42] the catalytic role played by the proton, which is a strong acid in an aqueous medium, in organic chemistry is frequently assumed in organofluorine chemistry by the fluoride ion, which is a strong base in an aprotic medium.[1]

One example of the reversal of the mechanism is the opoxidation of fluoro-olefins by peracids discovered by Knunyants and co-workers:[43,44] methyl perfluoromethacrylate and also its derivatives are readily epoxidised by *p*-nitroperbenzoic acid in absolute ether at room temperature, but in this case the Prilezhaev reaction proceeds via a nucleophilic mechanism as a consequence of the exceptionally high electrophilicity of the perfluoromethacrylic acid ester.

The sensitivity of fluoro-olefins to electrophilic attack is low, so that their oxidation via an electrophilic mechanism is hindered. The only instance of the epoxidation of fluoro-olefins via an electrophilic mechanism is oxidation by potassium permanganate in anhydrous hydrogen fluoride at 203 K:[45]

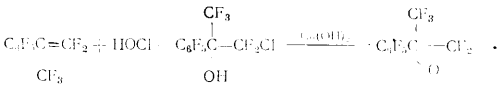


The reaction proceeds via a stage involving electrophilic attack by manganic acid fluoride on the double bond:[45]

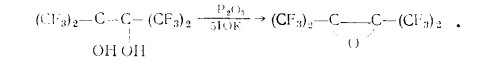


The ionic oxidation reactions of fluoro-olefins examined are characterised by a high rate and take place under mild conditions in reactive polar solvents (water, alcohols, HF, etc.) using as oxidants compounds with active oxygen (H_2O_2, $KMnO_4$, metal hypohalites, and peracids). The complete absence of polymeric products with perfluoropolyether and perfluoropolyperoxide structures, characteristic of radical oxidation reactions of fluoro-olefins, is striking. Overall, the ionic oxidation reactions of fluoro-olefins are characterised by a much lower selectivity of the epoxidation compared with the electrophilic epoxidation of hydrocarbon olefins.

The method of synthesis of fluorocarbon epoxides involving the dehydrogenation of halogenoalcohols in the presence of aqueous solutions of alkalies on brief (5–10 min) heating to 348–373 K has been developed:[119,120]



The epoxide is also formed on dehydration of perfluoropinacol:[21]



However, only the syntheses of fluorocarbon epoxides via fluoro-olefin oxidation reactions are of practical importance.

III. ELECTROCHEMICAL AND HETEROGENEOUS-CATALYTIC OXIDATION OF FLUORO-OLEFINS

In terms of their conditions, the chemical nature of the oxidants employed, and the character of the products formed, the reactions indicated occupy an intermediate position between ionic and radical oxidation reactions of fluoro-olefins. Metallic silver is known to have unique catalytic activity in relation to the epoxidation of ethylene by oxygen.[46–48]

Tetrafluoroethylene is also oxidised by oxygen in the presence of a silver catalyst with formation of epoxytetrafluoroethane (ETFE), carbonyl difluoride (CDF), and small amounts of perfluorocyclopropane and oligomers with a poly(difluoromethylene oxide) structure. Below 400 K, TFE is not oxidised in the presence of silver, but at a higher temperature virtually the only oxidation products are ETFE and CDF, i.e. the reaction proceeds via two pathways like the oxidation of ethylene:[47]

$$CF_2{=}CF_2 + \frac{1}{2}O_2 \rightarrow CF_2{-}CF_2{-}158\ \text{kJ}; \quad (2)$$

$$CF_2{=}CF_2 + O_2 \rightarrow 2COF_2 - 614\ \text{kJ}. \quad (3)$$

In the range 403–433 K, there is a virtually linear increase of the rates of formation of ETFE and CDF with increase of temperature (Fig. 2) accompanied by a constant selectivity of the epoxidation in the range 55–67 vol.%,[49] which agrees with the selectivity of the epoxidation of ethylene in the presence of silver.[45–47] The optimum temperature of the epoxidation of TFE in the presence of silver is 410–430 K,[49] i.e. appreciably below the optimum temperature of the epoxidation of ethylene, which is in the range 500–570 K;[45–47] with increase of temperature, CDF becomes the only product.

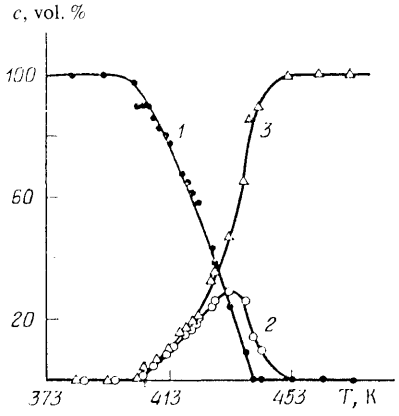


Figure 2. Temperature variation of the composition of the products of the heterogeneous-catalytic oxidation of TFE by atmospheric oxygen in the presence of a granulated silver catalyst in a flow reactor at atmospheric pressure, for the molar ratio O_2 : TFE = 1.2, and at a space velocity of the supply of TFE of 1.1 min^{-1}: 1) TFE; 2) ETFE; 3) CDF.[49]

The above data indicate a higher catalytic activity of silver in the epoxidation of TFE compared with the epoxidation of ethylene. This conclusion agrees well with the mechanism of the epoxidation in the presence of silver: TFE is much more active than ethylene in reactions with nucleophiles,[25] which facilitates its reaction with oxygen chemisorbed on the surface of silver in the form of the peroxide anion, which is the epoxidising agent.[45,46,50]

The activation energies for the epoxidation of TFE [reaction (2)] and the formation of CDF [reaction (3)] in the presence of the silver catalyst in the temperature range 408–433 K are respectively 100 ± 18 and 128 ± 35 kJ mol^{-1}, i.e. they exceed somewhat the activation energies for the analogous stages in the oxidation of ethylene:[49] and 80 and 90 kJ mol^{-1}.

The carbonyl difluoride formed in the oxidation of TFE is a highly active fluorinating agent,[1] so that the silver catalyst is poisoned as a result of the formation of surface silver fluorides.[48] The silver catalyst fully deactivated in relation to the reaction (2) behaves in reaction (3) analogously to inert quartz packing:[51] it does not initiate oxidation below 500 K; at 503 K a branched chain oxidation reaction with formation of CDF alone begins.

The heterogeneous-catalytic epoxidation of fluoro-olefins in the presence of silica gel,[52–54] which has no analogue in the chemistry of hydrocarbon compounds, is of interest. Before use as the catalyst, the silica gel is first activated at 448–673 K in a stream of air and the fluoro-olefin for 0.5 to 25 h. The oxidation is carried out in a flow reactor at atmospheric pressure, the space velocities at which the fluoro-olefin and the oxygen are supplied are 0.22 and 0.11 min^{-1}, and the optimum epoxidation temperatures are 463–498 K for HFP and 273–323 K for TFE. A yield of EHFP in excess of 80% relative to the HFP which has reacted is then attained for a conversion of 10–40%.[52–53] In the epoxidation of TFE the yield of the epoxide is more than 70% relative to the olefine which has reacted for a conversion of the latter of 40–90%.[54]

There are no data concerning the mechanism of the epoxidation of fluoro-olefins in the presence of silica gel, the process is poorly reproducible, and silica gel decomposes vigorously during activation and oxidation owing to its reaction with CDF with formation of gaseous CO_2 and SiF_4. In the activation of silica gel there is a possibility of partial conversion of surface SiOH groups into the hypofluorite groups SiOF, which can initiate radical oxidation.[54]

The electrochemical epoxidation of HFP in 80% acetic acid, acetonitrile, and an alkaline solution of sodium perchlorate using a perfluorinated ion-exchange membrane of the "nafion" type for the separation of the cathodic and anodic compartments occupies an intermediate position as regards conditions and mechanism.[55–56] At 293 K, atmospheric pressure, and a current density of 10–50 mA cm^{-2} the process is characterised by a selectivity of the epoxidation of 45–65% for a conversion of HFP of 30–50%; the current yield is 20–35% and the side products are CO_2, HF, and C_2F_5COOH.

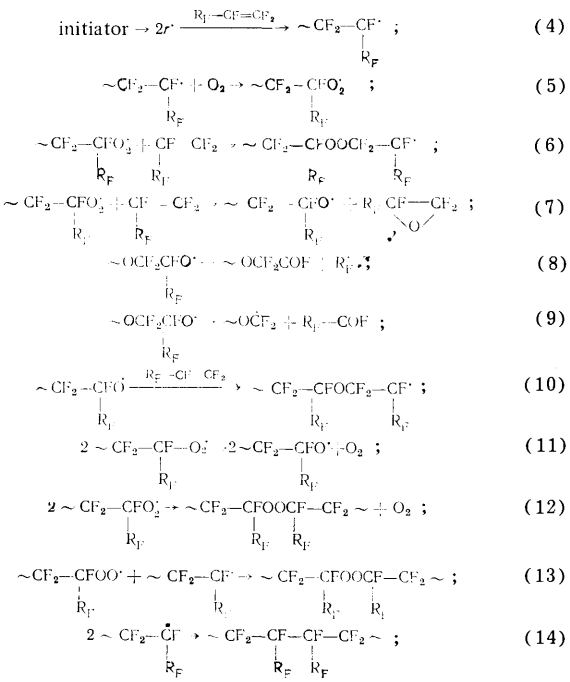
IV. OXIDATION OF FLUORO-OLEFINS VIA A RADICAL MECHANISM

Terminal fluoro-olefins are readily oxidised by molecular oxygen in both gas and liquid phases. There is at present no doubt about the fact that the oxidation of fluoro-olefins proceeds via a free-radical chain mechanism involving a large number of elementary chain propagation and termination stages and also a stage in which the free radicals decompose and which leads to the formation of non-radical products. The composition of the products and the mechanism of the oxidation of fluoro-olefins therefore vary within wide limits depending on the process conditions. For chain oxidation reactions, the selectivity is a function of the chain length, the degree of conversion, and process conditions (solvent, temperature, surface of reaction vessel) and depends on the constants for the elementary stages of the process and also on the concentrations of the substances involved in the chemical reaction.[58]

The mechanism of the oxidation of perfluoro-olefins differs little from the mechanism of the oxidation of unsaturated hydrocarbon analogues. In fluoro-olefins the C–F bond,

whose energy is 448–485 kJ mol^{-1},[1,59] is stronger than the C–H or C–C bond and the oxidation therefore proceeds directly at the double bond and not at the C–F bond. The process is more selective and proceeds with a much smaller number of side products than in the oxidation of olefins, where reaction takes place via a stage in which the hydrogen atom is abstracted preferentially from the α-position relative to the double bond of the olefin.[60,61] The oxidation of fluoro-olefins results in a formation of carbonyl-containing products with a smaller number of carbon atoms than in the initial olefin (acyl fluorides, ketones) and oligomeric products with a perfluoropolyether and perfluoropolyperoxide structures. The C-F bond is also not involved in the formation of these products.

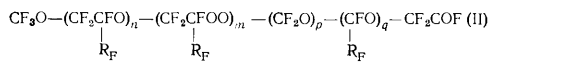
The composition of the products indicates the applicability in the oxidation of fluoro-olefins of the Mayo–Sianesi scheme, which treats oxidation as the simultaneous radical copolymerisation of the olefin and oxygen and the decomposition of the growing radicals:[62,63]



where R_F = F, perfluoroalkyl, or perfluoroalkoxy-group and $\dot{r}$ is the initiator radical.

Only terminal fluoro-olefins are oxidised via a radical mechanism.[10–13] Internal and cyclic fluoro-olefins are almost inert to radical oxidation, which agrees with their low reactivity in radical polymerisation.

The initiated oxidation of terminal fluoro-olefins proceeds already at a temperature below 273 K with the predominance of stages (5) and (6), characterised by a lower activation energy compared with the stages leading to the formation of the epoxide and acid fluorides [stages (7)–(9)]. The main products of the low-temperature oxidation are oils with the perfluoropolyether and perfluoropolyoxide structures having the general formula[13]



Perfluoroalkyl radicals combine with oxygen much faster than the fluoro-olefin molecule and for this reason blocks consisting of several fluoro-olefin fragments are absent from the polymer.[63] The low-temperature oxidation of fluoro-olefins is initiated by ozone,[64,65] oxygen difluoride,[66] etc. The low-temperature oxidative polymerisation of fluoro-olefins under the influence of ultraviolet radiation, which, apart from initiation, induces the conversion of the peroxy-groups into ether groups in the polymer formed, is technologically the most effective.

The oxidative photopolymerisation of fluoro-olefins is carried out in the temperature range from 173 to 353 K and the optimum oxidation temperature for TFE and HFP is 263 K.[67,68] Pressure is used only to keep the fluoro-olefin in the liquid state.[67]

The oxidation proceeds via a free-radical chain mechanism with degenerate chain branching. Chain branching takes place as a result of the photolysis of the perfluoroacyl fluoride and peroxides which have accumulated during the reaction as a result of photolysis. The quantum-chemical yield of the oxidative photopolymerisation of fluoro-olefins is in the range from 10 to 85.[63,69] The radiation-chemical yield in the oxidative polymerisation of HFP at 300 K under the influence of ^{60}Co γ-rays exceeds 160.[70] The effective activation energy for the oxidative photopolymerisation of perfluorinated alkyl vinyl ethers 2.1–4.2 kJ mol^{-1}.[69] In initiation by ultraviolet light, radiation with wavelengths in the range 2600–3200 Å is the most effective;[63] radiation with wavelengths below 2600 Å induces the preferential formation of peroxy-groups, while longer-wavelength radiation promotes the formation of the perfluoropolyether structure.[71]

Fluoro-olefins and oxygen hardly absorb the ultraviolet light from mercury quartz lamps; in practice sensitisers are not used in liquid-phase photochemical oxidation. The reaction begins after a short induction period during which a small amount of products having the perfluorodialkyl peroxide and perfluoroacyl fluoride structures accumulate in the system and subsequently initiation takes place as a result of the photolysis of these compounds.[63] The applicability of scheme (4)–(14) to the description of the kinetics of the oxidative photopolymerisation of fluoro-olefins has been demonstrated by Sianesi and has been discussed in two communications.[9,13]

Only the oxidative photopolymerisation of TFE [72–76] and HFP [63,67,77–79] is of practical value and the main bulk of publications have been devoted to the development of the process in relation to these two monomers. The oxidative photopolymerisation of HFP is carried out in the bulk of the olefin, the yield of the transparent viscous product having structure (II) exceeds 90%, the average degree of polymerisation is 30–40 units, the hexafluoropropylene oxide units are joined mainly "head to tail",[63] and the side products are gaseous COF_2, CF_3COF, and EHFP.[67]

The oxidative photopolymerisation of TFE is carried out in an inert solvent, the yield of the viscous polymeric product having structure (II) and a molecular weight of 10^4–10^5 is 40–50%,[63] the distribution of the difluoromethylene oxide and tetrafluoroethylene units in the chain is random, the peroxy-groups are mainly linked to the CF_2–CF_2 units, and CDF and ETFE are formed as gaseous products.[63]

Oxidative photopolymerisation of HFP is a simple and cheap method of synthesising perfluoropolyether oils.[13,80] The ratio of the peroxide and ether units in the polymer is defined by the equation[63]

$$\frac{m}{n} = \frac{k_{13}\,[\mathrm{HFP}]}{2\,(1 + k_{11}/k_{12})\,k_{12}^{1/2} I^{1/2}},$$

where k_{11}, k_{12}, and k_{13} are the rate constants for the elementary stages and I is the density of the radiation.

With increase of the temperature of the initiated oxidation of fluoro-olefins, stages (7)–(9) involving the decomposition of the growing radicals, which have higher activation energies than stages (5) and (6), become dominant. As a consequence of this, the yield of the polymeric products with structure (II) falls, the molecular weight decreases, fragments of the difluoromethylene oxide structure predominate in the polymer, and the yield of the epoxide and the carbonyl-containing products, formed as a result of oxidation with rupture of their double bond, increases.[63] In the range 370–420 K the main fluoro-olefin oxidation product is the epoxide, while at temperatures above 470 K the products resulting from the dissociation of the double bond are virtually the only ones.

By studying the kinetics of the low-temperature oxidation of HFP in the gas phase and using the principle of the quasi-stationary concentrations of free radicals, it has been shown on the basis of the scheme presented above[13] that the rate of reaction is described by the equation

$$\frac{d[O_2]}{dt} = \frac{1}{2}\left(1 + \frac{k_{11}}{k_{12}}\right) I \text{ and } \frac{d[HFP]}{dt} = \frac{1}{2}\frac{k_{11}}{k_{12}} I ,$$

while the rate of the photochemical low-temperature oxidation of HFP in the liquid phase is given by the equations

$$-\frac{d[O_2]}{dt} = \left(1 + \frac{k_{11}}{k_{12}}\right) I + k_{13}(I/k_{12})^{1/2}[HFP] ,$$

$$-\frac{d[HFP]}{dt} = 2\left(\frac{k_{11}}{k_{12}}\right) I + k_{13}(I/k_{12})^{1/2}[HFP] ,$$

The equations for the rates of formation of the epoxide (w_e) and carbonyl-containing oxidation products formed with dissociation of the double bond (w_c) from the fluoro-olefin (M) are as follows:

$$w_e = k_7[M]\left(\frac{w_i}{S}\right)^{1/2} , \quad (15)$$

$$w_c = (k_9 + k_8)\frac{k_7[M](w_i/S)^{1/2} + k_{11}(w_i/S)}{k_5 + k_9 + k_{10}[M]} , \quad (16)$$

where w_i is the rate of initiation and

$$S = k_{12} + 2k_{13}\frac{k_6 + k_7[M]}{k_5[O_2]} + k_{14}\frac{(k_6 + k_7)^2[M]^2}{k_5^2[O_2]^2} . \quad (17)$$

Compared with the rate of formation of carbonyl-containing products [Eqn.(16)] the rate of epoxidation [Eqn.(15)] depends to a greater extent on the concentration of the olefin and to a lesser extent on the rate of initiation. The selectivity of the epoxidation in the radical oxidation reactions of fluoro-olefins therefore increases with increasing olefin concentration and with decrease of the rates of initiation.

At low oxygen concentrations, chain termination takes place mainly via reaction (14), the rates of reactions (12) and (13) can be neglected, and the expression for the rate of epoxidation becomes

$$w_e = \frac{k_7 k_5[O_2]}{k_{14}^{1/2}(k_5 + k_7)} \cdot w_i^{1/2} , \quad (18)$$

i.e. the rate of epoxidation is proportional to the concentration of oxygen and is independent of the concentration of the olefin.

At high oxygen concentrations, where the main chain termination reaction is reaction (12) and the rates of reactions (13) and (14) can be neglected, the expression for the rate of epoxidation becomes

$$w_e = k_7[M]\left(\frac{w_i}{k_{12}}\right)^{1/2} , \quad (19)$$

i.e. the rate of epoxidation is independent of the oxygen concentration and is proportional to the olefin concentration. Under these conditions, the effective activation energy for epoxidation E_{eff} is defined by the expression

$$E_{eff} = \frac{1}{2}E_i + E_7 - \frac{1}{2}E_{12} , \quad (20)$$

where E_i is the activation energy for the initiation stage and E_{12} the activation energy for the recombination of the peroxy-radicals, which is zero.[81] The initiated oxidation of fluoro-olefins by oxygen at an elevated temperature is carried out in a flow regime in the gas phase at atmospheric pressure; sometimes the volume of the reactor is filled with an inert solvent.

The photoinitiated oxidation is of practical interest as the most effective method of synthesis of ETFE. Among processes of this type, the gas-phase oxidation of TFE has been most thoroughly investigated. Here too radiation at a wavelength below 3200 Å is the most effective.[82] Sensitisers are used in this reaction: mercury vapour,[83] bromine, chlorine, nitrogen oxides, hydrogen bromide,[82] etc. Bromine is the most active in this series of sensitisers.

A biradical chain mechanism is feasible for the gas-phase photochemical oxidation of fluoro-olefins sensitised by mercury vapour:[83,84,86]

$$Hg \xrightarrow{h\nu} Hg^* \xrightarrow{C_2F_4} C_2F_4^* \xrightarrow{O_2} \dot{C}F_2\dot{O}_2 + \ddot{C}F_2$$

$$\dot{C}F_2\dot{O}_2 + C_2F_4 \rightarrow C_2F_4O + COF_2 ,$$

$$\dot{C}F_2\dot{O}_2 + \ddot{C}F_2 \rightarrow 2COF_2 .$$

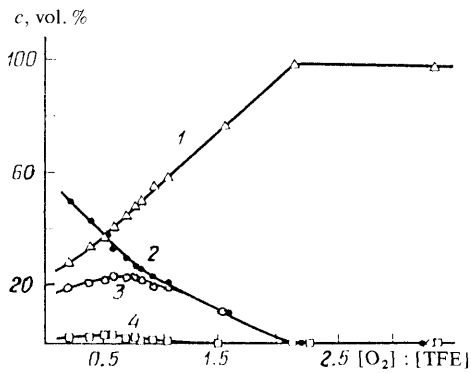


Figure 3. The influence of the molar ratio $[O_2]:[TFE]$ on the composition of the products of the gas-phase photochemical oxidation of tetrafluoroethylene by atmospheric oxygen at 365 K, at atmospheric pressure, and for a residence time in the reaction zone of 1.5 min and the molar ratio $Br_2:TFE = 2 \times 10^{-4}$: 1) CDF; 2) TFE; 3) ETFE; 4) perfluorocyclopropane.[87]

The gas-phase oxidation of TFE by oxygen in a flow reactor at atmospheric pressure, a temperature of 370–400 K, for the molar ratio $O_2:TFE = 0.8$, for a residence time of the reactants in the reaction zone of 1.5 min, and for a power of a moderate pressure mercury quartz lamp of 1395 W is characterised by yields of ETFE of 21–23% relative to the TFE which has reacted for a conversion of the latter of 65–70% (Fig.3).[82,87] CDF is a side product in the process

and the yield of oligomeric products does not exceed 5%.[82] The oligomeric products formed at an elevated temperature have the poly(difluoromethylene oxide) structures (III) and (IV) [88,89] with a low content of peroxy-groups:

$$CF_3O-(CF_2O)_n-CF_2COF \quad (III) \qquad CF_3O-(CF_2O)_n-COF \quad (IV)$$

The structure of the oligomers is determined by the lower rate of decomposition of the corresponding alkoxy-radicals ($\sim CF_2OCF_2O^{\cdot} \rightarrow \sim CF_2O^{\cdot} + COF_2$) compared with the rates of reactions (8) and (9), because the dissociation energy of the C–O bond in perfluoropolyethers (418 kJ mol^{-1}) [10] exceeds significantly the energy of the C–C bond, which is 338–376 kJ mol^{-1}.[10]

The oxidation reactions of fluoro-olefins are much more exothermic than the oxidation reactions of olefins. The exothermic effect in the oxidation of TFE to CDF is 614 kJ mol^{-1}, while in the analogous reaction involving the oxidation of ethylene to formaldehyde 286 kJ mol^{-1} is evolved.[90] The energetic stabilisation of the reaction products is therefore important in the fluoro-olefin oxidation reactions designed to obtain incomplete oxidation products, particularly expoxides. Thus, in the oxidation of TFE or HFP by atomic oxygen in the gas phase, the excited epoxide molecules formed initially do not have enough time for stabilisation and decompose with formation of CDF and difluorocarbene.[84–86]

The increase of the efficiency of the energetic stabilisation of the products resulting from the oxidation being carried out in the liquid phase leads to an increase of the yield of the epoxide. The photochemical oxidation of TFE by oxygen at 390 K in a flow regime with the reactor volume filled by an inert perfluorinated solvent makes it possible to raise the yield of TFE to 60–70% relative to the TFE which has reacted.[11,12,82] This process is one of the most effective methods of synthesis of TFE and is used as a preparative method for this purpose.[11,12] However, judging from the existing publications, there is as yet no industrial manufacture of ETFE by this procedure.

The radical oxidation of fluoro-olefins via scheme (4)–(14) is effectively initiated, apart from ultraviolet radiation, by ionising radiation, ozone, and oxygen difluoride.

The radiation-chemical oxidation of fluoro-olefins in the gas phase at an elevated temperature leads to the formation of an epoxide, carbonyl-containing products of oxidation with rupture of the double bond, and a small amount of polymers having the difluoromethylene oxide structures (III) and (IV).[82,91] An increase of the hardness of the ionising radiation reduces the yield of the epoxide and the degree of conversion of the olefin:[91] a fall of temperature entails a decrease of the degree of conversion and of the relative yield of gaseous products,[91] but the ratio of the yields of CDF and the epoxide remains constant under these conditions; an increase of the pressure entails some increase of the rate of the gas-phase radiation-chemical epoxidation of TFE,[92] the yield of the epoxide diminishing with increase of the oxygen : olefin ratio.[92] The radiation-chemical yield of the gas-phase oxidation of TFE and chlorotrifluoroethylene by molecular oxygen at room temperature and atmospheric pressure and under exposure to X-rays (50 kV) is in the range 900–3300.[74]

The gas-phase oxidation of fluoro-olefins by ozonised oxygen at room or an elevated temperature makes it possible to obtain epoxides in satisfactory yields. The oxidation of TFE by ozonised oxygen in a flow reactor at 288 K with the molar ratios $TFE:O_3 = 31.7$ and $TFE:O_2 = 1$ makes it possible to obtain ETFE in 46% yield relative to the TFE which has reacted for a conversion of the latter of 41.3%.[93] The yield of the polymeric products having structure (II) and a molecular weight of 1.5×10^3 is 19%.[93] The main structural unit of the polymer is CF_2O; the number of terminal CF_3O groups in the polymer is twice as large as the number of acid fluoride groups;[63] when the molar ratio $TFE:O_2$ is raised from 0.5 to 1.8, the number of peroxy-groups in the polymer falls from 5 to 3 per 100 CF_2O units; the content of C–C bonds in the polymer is then almost constant and is 5–6 bonds per 100 CF_2O units.[63]

It is possible to epoxidise TFE with pure ozone at 273 K, whereupon the yield of the epoxide is 50% for the molar ratio $O_3:TFE = 0.01$,[94] but, with increase of this ratio, the yield of the epoxide falls sharply and for the molar ratio $O_3:TFE = 1$ virtually the only product is CDF.[94]

Tetrafluoroethylene reacts readily with OF_2 in the dark to form an equimolar mixture of CF_4 and CDF; ETFE was not then detected.[95] Under the influence of ultraviolet radiation, the main reaction product is the epoxide.[21,95] For example, irradiation of a mixture of HFP and OF_2 with quartz ultraviolet light in the gas phase at room temperature in the course of 12 h leads to a yield of EHFP of 42% for a conversion of HFP of 57%.[95]

Catalytic epoxidation of fluoro-olefins by oxygen difluoride in the presence of silver difluoride is also known.[21,96] The reaction is carried out in a stainless steel flow reactor in the gas phase or in the presence of an inert solvent for the molar ratio OF_2 : olefin = 1 : 1 (at 333 K); the yield of the epoxide in the oxidation of HFP is 23 vol.%.[96]

In the presence of molecular oxygen OF_2 is an effective initiator of the oxidation of fluoro-olefins and the main oxidation product is the epoxide.[97]

The oxidation of fluoro-olefins initiated by oxygen difluoride proceeds at a temperature as low as 238–253 K; with increase of temperature, the rate of reaction increases and becomes technologically acceptable, starting from room temperature. The optimum epoxidation temperature depends on the chemical nature of the olefins and is in the range between room temperature and 393 K. The process is characterised by a series of kinetic features inconsistent with the Mayo–Sianesi scheme defined by Eqns.(4)–(14). Under the otpimum conditions, the yield of the epoxide exceeds 90%,[97] while according to the Mayo–Sianesi scheme the selectivity of the epoxidation should not exceed 67 vol.%.[62] The main side products are CDF, perfluoroacetyl fluoride, and small amounts of a polymeric product.[97] With increase of the amount of OF_2 introduced into the reaction mixture, the rate of oxidation and the yield of the epoxide relative to the olefin which has reacted also rise, which likewise conflicts with the Mayo–Sianesi scheme [see Eqns.(15) and (16)]. For example, in the oxidation of 6-monohydroundecafluorohex-1-ene in bulk at 393 K in the course of 4 h, an increase of the amount of OF_2 supplied to the reactor from 1.6 to 1000 ml per 1000 ml of oxygen leads to an increase of the degree of conversion of the olefin from 87.8 to 100% and to an increase of the yield of the epoxide from 59.4 to 92% relative to the olefin which has reacted.[97] The above features of the process show that, in the presence of oxygen, oxygen difluoride behaves not only as an initiator but also as a highly effective epoxidising agent.

The epoxidation with the $OF_2 + O_2$ mixture is more selective and proceeds steadily in the liquid phase, in the bulk of the olefin, or in an inert solvent.[97]

The formation of only products of oxidation with rupture of the double bond [polymeric products having structures (III) and (IV)] in the absence of epoxides is characteristic of the thermal or initiated oxidation of fluoro-olefins by oxygen in the gas phase at temperatures above 473 K.[72,98–100] The reaction of TFE with the oxygen in a shock wave results in the formation of CO_2, CF_4, C_2F_6, etc. together with CDF, but ETFE is absent.[101]

When the thermal oxidation of fluoro-olefins with oxygen is carried out in the liquid phase, the epoxide is formed as the main product; in addition, carbonyl-containing products of oxidation with rupture of the double bond and oligomeric products having structures (III) and (IV) are formed.[102-105] The oxidation is carried out at 320–520 K, the optimum temperatures for the epoxidation of different fluoro-olefins not being the same:[102] they are 348 K for chlorotrifluoroethylene, 360–380 K for TFE, and 400–420 K for HFP.

It is best to keep the molar ratio O_2:olefin below unity, since in the presence of an excess of oxygen the yield of the epoxide is reduced.[102] The solvents employed are perhalogenated compounds, for example, $CF_2ClCFCl_2$, CCl_4, etc. In order to maintain the fluoro-olefin in the liquid phase, the oxidation is carried out at an elevated pressure.

The thermal liquid-phase oxidation of fluoro-olefins is a degenerate-branched chain process, which is indicated by the S-shape of the kinetic curves (Fig.4), the complete supporession of the oxidation following the addition of inhibitors, even weak ones such as quinone or nitroxy-radicals, and the elimination of the induction period on treatment with initiators even at 50 °C (in the absence of an initiator, the oxidation becomes appreciable only at temperatures above 100 °C after a prolonged induction period).[106]

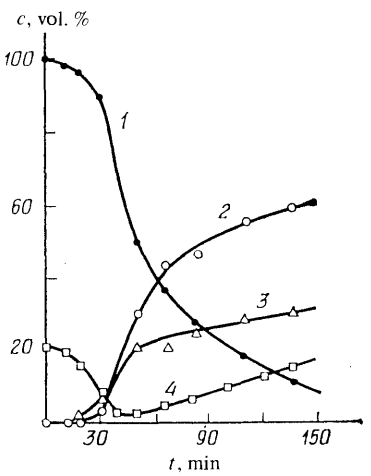


Figure 4. Kinetic curves for the thermal liquid-phase oxidation of HFP by compressed air (rate of supply 9 litre h^{-1}) in Khladon-113 at an initial HFP concentration of 0.13 M, 423 K, and a pressure of 5 MPa: 1) HFP; 2) EHFP; 3) trifluoroacetyl fluoride; 4) O_2 content in effluent gases from the reactor.[109]

The branching agents are the oligomeric peroxy-compounds with structures (III) and (IV) formed.[106,107] The chemical and nature of the solvent, the material of the reactor, and the state of the walls exert a marked inlfuence on the yield of the epoxide and other oxidation products.

The metallic surface of the reaction vessel has a catalytic effect on reactions leading to the formation of acid fluorides and oligomeric products, the selectivity with respect to the epoxide being reduced.[106] In stainless steel reactors in Freon-113, the yiled of EHFP does not exceed 40–50% relative to the HFP which has reacted, while in PTFE reactors the yield of the epoxide reaches 70–80%.[106,107] The effect of the reactor walls is reduced when the solvents employed are highly viscous liquids, consisting of mixtures of aliphatic fluorocarbons and perfluorinated ethers,[106] owing to the decrease of the rate of diffusion of the species decomposing on the wall.

In contrast to the low-temperature photoinitiated oxidation of TFE and HFP, where the rate of reaction and the selectivity are independent of the ratio of the oxygen and olefin concentrations and depend solely on the radiation intensity,[13] the ratio of the rates of accumulation of the corresponding epoxides and acyl fluorides in the thermal oxidation increases linearly with increase of the fluoro-olefin concentration[109] and diminishes with increase of the initial O_2 concentration.[110] A decrease of the selectivity with respect to the epoxide as a function of the O_2 concentration has also been observed in the oxidation of a number of olefins:[62,111]

$$\frac{w_{ox}}{w_{ol}} = \frac{1}{A + B[O_2]}, \qquad (21)$$

where w_{ox} is the rate of formation of the olefin oxide, w_{ol} the rate of consumption of the initial olefin and A and B are constants which incorporate the ratios of the rate constants for the elementary stages. In most cases this type of relation is observed only over a certain part of the O_2 concentration range.

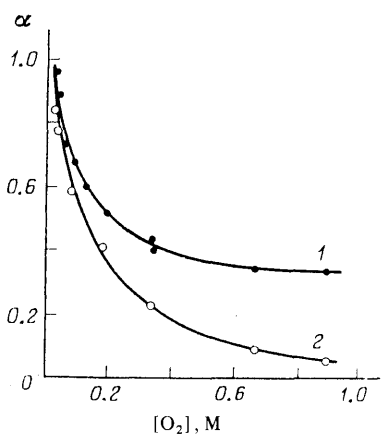


Figure 5. Dependence of the selectivity of the epoxidation α of perfluoro-octene (curve *1*) and HFP (curve *2*) on the initial O_2 concentration.[110]

At initial O_2 concentrations appreciably less than the initial fluoro-olefin concentration, the selectivity with respect to the epoxide is close to 100% and falls sharply with increase of the O_2 concentration, tending to a definite limit, which depends on the nature and length of the hydrocarbon chain of the fluoro-olefin (Fig.5). It follows from Table 1 that the oxidation of TFE in an excess of oxygen yields only COF_2 and a polymer, while in the oxidation of HFP and perfluoro-octene the yields of the corresponding epoxides reaches 20 and 36% with respect to the consumed olefin.

These data show that the mechanism of the oxidation of olefins put forward in a number of studies[4,14,62] cannot account either for the limit in the selectivity with respect to

the oxide on further increase of the O_2 concentration or for the high yields of the epoxides. It permits a theoretically feasible yield not greater than 66%, whereas in the oxidation of certain olefins and fluoro-olefins containing more than two carbon atoms their selectivity with respect to the epoxide reaches 70–100% for a conversion in an excess of 50%.[102,107,110,113] In order to explain such a high selectivity in the epoxidation of fluoro-olefins, the decrease of the process selectivity with increase of the O_2 concentration, and also the accumulation of equimolar amounts of CDF and acyl fluorides in which the number of carbon atoms is one less than in the initial olefin, the oxidation mechanism was supplemented[109] by the stage involving decomposition of the perfluoroperoxyalkyl radicals into two epoxide molecules:

$$RO_2-CF_2-\underset{\underset{R_F}{|}}{CF}OOCF_2\dot{C}F \rightarrow 2R_F\underset{\diagdown O \diagup}{CF}-CF_2 + R\dot{O}_2 \ , \qquad (22)$$

and also a stage involving the isomerisation and decomposition of the perfluoroalkylperoxy-radicals with rupture of the carbon skeleton:[106]

$$RO_2CF_2-\underset{\underset{R_F}{|}}{CF}-O\dot{O} \longrightarrow RO_2-CF_2-\underset{\underset{O-O}{\diagdown\diagup}}{CF}-R_F \longrightarrow R\dot{O}_2 + R_FCOF + COF_2 \qquad (23)$$

Table 1. Dependence of the yield of the epoxide on the length of the carbon chain of the fluoro-olefin for the ratio O_2 : fluoro-olefin = 3.

Fluoro-olefin	T, K	α, %	Refs.
C_3F_4	265	0	[112]
C_3F_6	393	20	[114]
C_8F_{16}	370	36	[110]

Notation: T is the oxidation temperature and α the yield of the fluoro-olefin oxide.

This pathway, leading to the formation of acyl fluorides, is dominant for long oxidation chains. If the chains are short, then the reaction of perfluoroalkoxy-radicals, formed in a quadratic interaction of the perfluoroalkylperoxy-radicals [reactions (8) and (9)], makes a significant contribution to the overall rate of formation of acyl fluorides:

$$RO_2-CF_2-\underset{\underset{R_F}{|}}{CF}\dot{O} \xrightarrow{O_2} \begin{cases} \longrightarrow RO_2-CF_2-COF + R_F\dot{O}_2 \ , \\ \longrightarrow RO_2-CF_2O\dot{O} + R_FCOF \ , \end{cases}$$

$$R_F = CF_3, \ldots C_nF_{2n+1} \ .$$

This regime is attained at high rates of initiation comparable to the rate of oxidation (chain length ≤ 10 units). In the liquid-phase oxidation of HFE a linear dependence of the ratio of the rate of accumulation of the sum of perfluoroacetyl fluoride and CDF to the rate of formation of EHFP on the square root of the rate of initiation is observed.[114] It is known that an excess of oxygen in free radical oxidation reactions results in the predominance of the system of $R\dot{O}_2$ radicals[60] which cannot produce the epoxide if one adopts the mechanism of the epoxidation of fluoro-olefins and the formation of perfluoroacyl fluorides [reactions (22) and (23)] presented above. However, in the oxidation of perfluoro-octene even at high oxygen concentrations (Fig.5) the formation of epoxyperfluoro-octane is observed (up to 40 mole % relative to the perfluoro-octene which has reacted).

In order to account for the observed limit in the selectivity of the expoxidation of fluoro-olefins as the O_2 concentration increases, it has been suggested that, as in the oxidation of the usual olefins,[113] a molecular epoxidation mechanism as well as the radical mechanism can operate in the oxidation of fluoro-olefins.[110] One of the possible pathways in the non-radical epoxidation mechanism is apparently the interaction of the cyclic peroxide formed via a radical mechanism:[113,115]

$$RO_2-CF_2-\underset{\underset{R_F}{|}}{CF}O\dot{O} \rightarrow R\dot{O}_2 + R_F-\underset{\underset{O-O}{\diagdown\diagup}}{C}-CF_2 \ , \qquad (24)$$

On the one hand, this peroxide can react with a second fluoro-olefin molecule to produce two epoxide molecules and, on the other, it can decompose into perfluoroacetyl fluoride and COF_2:

$$R_F-\underset{\underset{O-O}{\diagdown\diagup}}{\overset{F}{\overset{|}{C}}}-CF_2- \longrightarrow R_F-COF + COF_2 \ , \qquad (25)$$

$$\xrightarrow{R_FCF=CF_2} 2R_F-\underset{\diagdown O \diagup}{CF}-CF_2 \ . \qquad (26)$$

The introduction of a molecular mechanism of the epoxidation of fluoro-olefins made it possible to explain virtually all the observed kinetic features: the high selectivity of the epoxidation, the appearance of a limit in the selectivity with respect to the epoxide as the initial O_2 concentration increases, the formation of equimolar amounts of CDF and perfluoroacyl fluoride containing a smaller number of carbon atoms than in the initial olefin, and also the influence of the reaction vessel wall, which catalyses the decomposition of the above peroxides and the peroxy-radicals with dissociation of the C–C bond.

High-temperature oxidation by molecular oxygen in order to obtain epoxides is possible only for terminal fluoro-olefins, while internal and slight fluoro-olefins do not give rise to epoxides.[102] The oxidation of TFE and chlorotrifluoroethylene by this method is difficult to achieve for technical reasons owing to the risk of explosion. Thermal liquid-phase epoxidation of HFP is a highly effective method of synthesis of EHFP;[10] the process has been carried out by the Dupont Corporation[10,103,104] in a stainless steel autoclave in a continuous regime at 430 K, at a pressure of 2.8 MPa, and for the molar ratio O_2 : HFP = 0.6. The solvent employed was Khladon-113. After 20 min, up to 70% conversion of HFP is attained and the yield of the epoxide is more than 70%.[102,104]

Apart from the fluoro-olefin oxidation reactions, fluorocarbon epoxides can be obtained by other methods, for example by the addition of difluorocarbene to ketones or acyl fluorides:[116–118]

$$CF_3COCF_3 + \ddot{C}F_2 \rightarrow (CF_3)_2\underset{\diagdown O \diagup}{C}-CF_2 \ ,$$

$$CF_3COF + \ddot{C}F_2 \rightarrow CF_3-\underset{\diagdown O \diagup}{CF}-CF_2 \ .$$

Analysis of the patent and scientific literature shows that the fluoro-olefin oxidation processes can be readily achived, have many kinetic features distinguishing them from olefin oxidation processes, and make it possible to obtain fluorocarbon epoxides and perfluoropolyethers in high yields from readily available starting materials.

V. CHARACTERISTIC FEATURES OF THE PHYSICOCHEMICAL PROPERTIES AND MAIN APPLICATIONS OF THE FLUORO-OLEFIN OXIDATION PRODUCTS

In contrast to hydrocarbon epoxides, which have significantly higher boiling points than the corresponding olefins, the boiling points of fluorocarbon epoxides are close to those

of the corresponding fluoro-olefins (Table 2), which greatly hinders their separation. ETFE, whose boiling point differs considerably from that of TFE, is an exception; their mixture can therefore be comparatively readily separated by distillation. Under industrial conditions, extractive distillation of a mixture of EHFP and HFP in the presence of substituted benzenes, carbon tetrachloride, chloroform, etc. is recommended.[126,127]

Table 2. Certain physical constants of the epoxides and the corresponding olefins.

Compound	T, K*	Absorption band, cm^{-1}	Refs.
$CF_2—CF_2$ (O)	209.5 211	— 1610	[82, 91] [121]
$CF_2=CF_2$	197	—	[122]
$CH_2—CH_2$ (O)	283.7	1270	[123]
$CH_2=CH_2$	169	—	[124]
$CF_3CF—CF_2$ (O)	245	1550	[3,9]
$CF_3CF=CF_2$	243	—	[122]
$CH_3CH—CH_2$ (O)	307	1266	[123]
$CH_3CH=CH_2$	225	—	[124]
$CF_2—CFCl$ (O)	251	1540	[121, 125]
$CF_2=CFCl$	246	—	[122]
$(CF_3)_2C—CF_2$ (O)	276	1500	[3]
$(CF_3)_2C=CF_2$	280	—	[122]
$CF_2—CF(CF_2)_4—CF—CF_2$ (O, O)	377	1500	[31]
$CF_2—CF(CF_2)_4CF=CF_2$ (O)	378	1550	[31]
$CF_2=CF(CF_2)_4—CF—CF_2$ (O)	379	—	[31]

*T = boiling point.

The fluorocarbon epoxide ring has an absorption band in the range 1460–1610 cm^{-1},[3,21,22] while the ring of the carbon epoxides absorbs in the range 1240–1260 cm^{-1}.[123]

Fluorocarbon epoxides hardly dissolve in water, diglyme, etc., but they are readily soluble in fluorocarbon solvents, Freons, etc.[10] In contrast to this, epoxyethane is miscible with water in all proportions and is readily soluble in many of the usual hydrocarbon solvents.[46]

Fluorocarbon epoxides are thermally less stable than their hydrocarbon analogues. For example, the thermal decomposition of epoxyethane begins at 620 K and is characterised by an activation energy of 209–238 kJ mol^{-1}.[46] Epoxytetrafluoroethane is stable only at a reduced temperature and it is recommended that it be stored at 195 K.[12] Even at room temperature, ETFE readily isomerises to trifluoroacetyl fluoride on the walls of the vessel.[12] Above 323 K, ETFE undergoes thermal decomposition:[30,118,128]

$$CF_2(O)CF_2 \rightarrow COF_2 + \ddot{C}F_2 ,$$

The reaction is of first order with respect to ETFE and the rate constant is given by[128]

$$k = 10^{13.7}\exp(-132000/RT)\,s^{-1}\ \text{(Ref.128)}$$

With increase of pressure, the rate of decomposition of ETFE also rises and in the liquid phase there is a possibility of the explosive decomposition of ETFE, the products being CF_4, COF_2, and carbon.[10,30]

The thermal stability of fluorocarbon epoxides depends significantly on their structure. For example, epoxyperfluorocyclopentane is stable up to 573 K.[30] EHFP decomposes above 420 K:[21,30,118]

$$CF_3CF(O)CF_2—CF_3COF + \ddot{C}F_2 ,$$

$$\ddot{C}F_2—\ddot{C}F_2 \rightarrow CF_2=CF_2 + CF_2(CF_2)CF_2 \rightarrow —(CF_2)_n— .$$

The thermal stability of fluoro-olefins is significantly greater than that of the corresponding epoxides. For example, HFP undergoes thermal decomposition above 820 K.[129]

As a consequence of the relatively high electron density at the oxygen atom of the hydrocarbon epoxide ring, its opening proceeds via a stage in which the proton attacks the oxygen atom with the intermediate formation of an oxonium cation.[123] The high electronegativity of fluorine lowers the susceptibility of the oxygen atom in the fluorocarbon epoxide ring to electrophilic attack and the opening of the latter takes place as a rule owing to nucleophilic attack on the β-carbon atom with the intermediate formation of an alkoxide anion:[3,9]

$$R_F—CF(O)CF_2 + A^- \rightarrow R_F—\underset{A}{CF}—CF_2O^- \rightarrow R_FCFCOF + F^- ;$$

A = anion.

The anionic polymerisation of fluorocarbon epoxides is of practical importance and its elementary chain propagation stage involves the opening of the epoxide ring by an alkoxide anion with formation of an addition product:[10]

$$CF_3CF(O)CF_2 \xrightarrow{F^-} CF_3CF_2CF_2O^- \xrightarrow{n\,C_3F_6O} F—(CFCF_2O)_n—CF_2CF_2O^-$$

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$C_2F_5COF + F^- \qquad F—(CFCF_2O)_n—CF_2COF + F^- .$$

The anionic polymerisation of fluorocarbon epoxides proceeds in an aprotic polar solvent in the presence of sources of fluoride ions.[10] A relatively low degree of polymerisation of the order of 70–100 is then attained,[10,130] which is due to the high probability of the stage involving chain transfer as a result of the elimination of a fluoride ion from the perfluoroalkoxy-anion.[10] There are at present no methods for the synthesis of high-molecular-weight solid polymers from perfluorinated epoxides,[10,13] which resembles the initial situation in the polymerisation of hydrocarbon epoxides.[131] After stabilisation, low-molecular-weight EHFP oligomers are used as working (functional) liquids and cooling agents.[10–12] EHFP and ETFE dimers and trimers are used to obtain highly effective surfactants[132,133] and fluorinated polyacrylates,[134] the latter being used to impart oil- and water-repellant properties to fabrics and paper and for the protection of steel, glass, etc. against corrosion.

The anionic polymerisation of EHFP has been achieved in the USA[10–12] on an industrial scale, the aim being to synthesise thermally and chemically stable perfluoropolyether

oils having the structure

$$F-(CF(CF_3)-OF_2O)_n-CF_2CF_3 \quad (n = 72)$$

and fluorocarbon solvents with the structure

$$F-(CF(CF_3)-CF_2O)_m-CFHCF_3 \quad (m = 1-9)$$

The oxidation of fluoro-olefins results in the formation of carbonyl-containing compounds; the property of these compounds of greatest practical importance is their ability to combine with EHFP via an ionic mechanism to form (after pyrolysis) perfluorinated alkyl vinyl ethers, for example:[135]

$$COF_2 + CF_3CF(O)CF_2 \xrightarrow[\text{diglyme}]{CsF} CF_3OCF(CF_3)COF \xrightarrow[ZnO]{570-600\,K} CF_3OCF=CF_2 .$$

Perfluorinated alkyl vinyl ethers readily copolymerise via a radical mechanism with a number of fluoro-olefins, for example, with TFE, to form a modified polytetrafluoroethylene of the type of PFA Teflon, capable of being worked by casting under pressure and by extrusion,[136] or fluororubbers.[14, 15,137-139]

Methods for the synthesis of perfluorinated alkyl vinyl ethers with functional groups in the ω-position have been developed on the basis of perfluorobisacyl fluorides and EHFP, for example:[140]

$$FOC-(CF_2)_n-COF + CF_3CF(O)CF_2 \xrightarrow[\text{diglyme}]{CsF} FOC-(CF_2)_n-CF_2OCF(CF_3)COF \rightarrow$$

$$\xrightarrow[470K]{Na_2CO_3} FOC-(CF_2)_{n+1}-OCF=CF_2 \xrightarrow[3)\,P_2O_5]{1)\,CH_3OH\ 2)\,NH_3} NC-(CF_2)_{n+1}-OCF=CF_2 .$$

Perfluorinated alkyl vinyl ethers with functional groups are used to synthesise vulcanisable perfluorinated rubbers.[138,140]

A method has been developed for the synthesis of perfluorinated alkyl vinyl ethers with a sulphonyl fluoride group (V) on the basis of TFE, SO_3, and EHFP:[141]

$$CF_2=CF_2 + SO_3 \xrightarrow{313K} FSO_2CF_2COF \xrightarrow[CsF,\ \text{diglyme}]{CF_2(O)CF_2} \rightarrow$$

$$\rightarrow FSO_2CF_2CF_2OCF(CF_3)CF_2OCF(CF_3)COF \xrightarrow[Na_2CO_3]{500K} FSO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2 .$$

(V)

Perfluorinated copolymers used for the preparation of thermally and chemically stable ion-exchange membranes of the type of "Nafion" for fuel cells[19] and electrolysers in the chlorine industry[142] are obtained by the copolymerisation of compound (V) with TFE.

Perfluoropolyoxa-alkylene dicyanides are obtained from perfluorobisacyl fluorides and fluoro-olefin oxides:[5,6]

$$FOC-R_F-COF + CF_2(O)CFX \xrightarrow[\text{diglyme}]{CsF} \rightarrow$$

$$\rightarrow FC(=O)CFX-(OCF_2CFX)_m-OCF_2R_FCF_2O-(CFXCF_2O)_n-CFXC(=O)F \rightarrow$$

$$\xrightarrow[3)\,P_2O_5]{1)\,CH_3OH\ 2)\,NH_3} NCCFX-(OCF_2CFX)_m-OCF_2R_FCF_2O-(CFXCF_2O)_n-CFXCN$$

where R_F is a perfluoroalkylene containing between 0 and 20 carbon atoms and X is usually F or CF_3.

Perfluoropolyoxa-alkylene dicyanides are used to synthesise perfluorinated triazine rubbers with improved frost resistance.[13]

Apart from the syntheses based on reactions with fluoride oxides, fluorocarbon carbonyl-containing compounds have many other applications of practical importance: CDF is used for the fluorination of the carbonyl group to CF_2 (Sheppard and Sharts [1]); surfactants and fire resistant and oil- and water-repellant substances for the impregnation of fabrics have been obtained from hexafluoroacetone;[143] CDF, hexafluoroacetone, and perfluoroaldehydes are used as monomers in radical copolymerisation,[13] etc.

Polymeric products of the oxidation of fluoro-olefins containing peroxy-groups are used for the initiation of radical polymerisation.[67,70,77]

The reduction of peroxy-groups in the above polymers (for example with hydrogen, metal hydrides, etc.[144]) leads to the formation of bifunctional linear perfluoropolyethers used as monomers in polycondensation processes and also as surfactants with high chemical and thermal stability,[70,72,91,98, 145,146] as emulsifying agents in the polymerisation of TFE,[144] and as water-repellant agents for the impregnation of fabrics.[98,145,146] Modified products of the decomposition of perfluoroperoxide polymers are also used in the last two cases.[146]

In order to stabilise them (to remove peroxy- and terminal acid fluoride groups), the polymeric products of the oxidation of fluoro-olefins are treated with fluorine at 370–620 K [147] and sulphur tetrafluoride,[98] are heated at 520 K,[70] are irradiated with ultraviolet light,[70] and are heated with alkali up to 420–620 K.[70,147]

The stabilised products with the perfluoropolyether structure obtained are employed as thermally and chemically stable oils and bases for greases, as dielectrics and heat exchangers,[70,72,98,145] and as plasticisers and solvents for fluorine-containing polymers.[91,145]

The main application of the products of the oxidation of fluoro-olefins is the introduction of oxygen-containing groups into fluorocarbon polymers. In this connection it must be emphasised that, in terms of the character of their influence on the properties of fluorocarbon polymers, the oxygen-containing groups can be divided into two categories. The first includes ether groups, whose influence is due to their chemical inertness and low potential barrier to rotation about the single C–O bond.[13-15] The introduction of ether groups into fluorocarbon polymers sharply reduces the rigidity of the polymer chains, which alters many physical properties associated with the flexibility of the macromolecules and in the first place decreases significantly the glass point, the thermal stability of the fluoropolymers remaining virtually unchanged under these conditions and lying in the range 520–570 K.[13-15] The electron-accepting properties of fluorocarbon alkyl groups and the *p,p*-conjugation of the unshared electron pairs of the heteroatom and the nearest fluorine atoms are responsible for the high chemical inertness of the perfluorinated ethers.[1,2,13] By virtue of this, fluorocarbon polymers with ether groups retain a high chemical stability. Thus perfluoropoly(propylene oxide) is stable in solvents such as liquid oxygen, N_2O_4, boiling concentrated nitric acid, and 90% hydrogen peroxide, in fluorinating agents such as gaseous fluorine (up to 470 K) and boiling ClF_3 and CoF_3 (up to 470 K), in strong acids such as concentrated H_2SO_4 (up to 590 K), P_2O_5 (up to 650 K), and BF_3 (up to 670 K), and in strong bases such as fused NaOH (up to 570 K), $(CH_3)_3N$ (up to 670 K), and $NaOCH_3$ (up to 650 K), in contact with metals, etc.[10,148] A consequence of the chemical inertness of perfluoropolyethers is their biological inertness and non-flammability.[11,12]

However, a certain degree of basicity of the ether groups in perfluoropolyethers remains and is manifested in reactions with Lewis acids, for example with $AlCl_3$ (even at 370 to 420 K) [2,149] and by a considerable decrease of the thermal stability of perfluoropolyethers in the presence of metals such as aluminium, titanium, and their alloys; the thermal stability

of oils of the type of "Fomblin" decreases under these conditions from 670 to 520 K,[149] while contact between fluorocarbon polymers and metal surfaces has almost no influence on their thermal stability.

Another manifestation of the residual basicity of the ether groups in perfluoropolyethers is an increase of the intermolecular interaction forces compared with fluorocarbon polymers, as a result of which perfluoropolyethers are readily soluble in fluorinated solvents while they remain insoluble in hydrocarbon solvents,[148,149] and expansion of the temperature range of their existence in the liquid phase[2] and a sharp improvement of their viscosity-temperature characteristics.[13]

When the carbon atoms in the α-position in ethers are incompletely fluorinated, a sharp impairment of the properties of the polymers is observed: the CF_2OCH_2 group is chemically less stable than the non-fluorinated ether bond, being particularly readily hydrolysed.[13]

The degree of modification of the properties of fluorocarbon polymers depends on the number of ether groups introduced into the main chain or into the side groups. The structure of the perfluoropolyether having a statistical distribution of the CF_2CF_2O and CF_2O units with the difluoromethylene oxide units predominating is optimal as regards the glass point and the viscous-temperature properties. Perfluoropolyether oils with the above structure are highly viscous and very stable at low temperatures:[13,63,150] their glass points are of the order of 120 K, their thermal stabilities are 600–630 K, and the temperature coefficients of their viscosity are low.

In terms of thermal stability, the optimum structure of perfluoropolyethers is that of perfluoropoly(ethylene oxide) $(CF_2CF_2O)_n$, whose thermal stability (770–820 K) [151] is unique for polymers with a flexible chain. The presence of difluoromethylene oxide groups in the perfluoropolyether chain lowers the thermal stability of the polymer, particularly on contact with metals.[13]

Reactive groups whose chemical reactivity is significantly higher than that of the analogous groups in hydrocarbon polymers belong to the second category of oxygen-containing groups introduced into fluorocarbon polymers by means of fluoro-olefin oxidation products. For example, the carboxy-groups are more acid and the carbonyl groups are more electrophilic,[1,152] as a result of which fluorinated polymers with functional groups in the main chain, for example, fluorine-containing polyesters, polyamides, polyurethanes, etc., have a low chemical stability, particularly in an alkaline medium.[13]

The introduction of reactive functional groups into fluorocarbon polymers as terminal or side groups imparts to the polymers a capacity for chemical vulcanisation, ion-exchange and catalytic activity, etc. These groups are introduced as a result of copolymerisation with fluoro-monomers containing a functional group in the ω-position.[5,140] The functional groups employed are COOH, COOR, $CONH_2$, CN, $CF-CF_2$ (with O), SO_2F, etc.[17,139–141,153]

After vulcanisation, the reactive functional groups usually no longer affect the chemical properties of the copolymer and their influence on the physical properties of the vulcanised material is manifested only owing to the increase of the strength of the cross-links.[139] However, the introduction of a large number of reactive functional groups induces a sharp change of both chemical and physical properties of fluoro-polymers. For example, a copolymer has been obtained from TFE and the sulpho-olefin (V), which exhibits not only an ion-exchange activity but also differs significantly from polytetrafluoroethylene in its physical properties: it swells in water to the extent of 25 wt.%[19] and dissolves in polar organic solvents such as ethanol, butanol, $C_6H_5N(CF_3)_2$, etc.[154]

Examination of the main applications of the products of the oxidation of fluoro-olefins shows that this reaction leads to key monomers for the synthesis of fluorine-containing polymers.

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Institute of Chemical Physics,
The USSR Academy of Sciences,
Moscow

Russian Chemical Reviews

August 1984

Translated from *Uspekhi Khimii*, 53, 1249-1279 (1984)

The Quantum Chemistry of Unusual Oxidation States of the Lanthanides and Actinides

V.I.Spitsyn and G.V.Ionova

The electronic structure and properties of the actinides in unusual oxidation states have been examined within the framework of quantum-chemical ideas. Hartree-Fock atomic calculations for the actinide series, and molecular orbital calculations for the octahedral oxyanions of uranium, neptunium, plutonium, and americium in high and highest oxidation states, and for the octahedral chloro-complexes of the actinides(III) and (IV) from protactinium to einsteinium, have been carried out. These calculations have been used to examine the possible existence of various new oxidation states of the actinides.
A cation-cation interaction mechanism has been proposed. The characteristic features of the *trans*-effect in the chemistry of the actinides have been examined. New possibilities for using the Mössbauer isomer shifts at the actinide nuclei to interpret chemical properties have been demonstrated. The influence of relativistic effects on the chemical properties of the actinides has been analysed. In particular, it has been shown that the high value of the spin-orbit splitting is responsible for the gradual stabilisation and stability of the bivalent state at the end of the actinide series, the significant difference in the stability of the lanthanides(IV) and actinides(IV), and the possibility in principle of obtaining lanthanyl groups at the end of the lanthanide series.
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I. INTRODUCTION

In recent years there has been a marked increase in interest in compounds of the *f*-elements, because of their varied practical applications. Practical requirements are making it necessary to carry out more detailed studies of "classical" compounds of the bivalent and tervalent lanthanides and actinides, and to prepare new compounds in new oxidation states. Lanthanides and actinides are interesting objects of research studies, since the question of the discovery of new oxidation states can now be raised for only a few elements of Mendeleev's periodic system.

Quantum chemistry plays an important role in the study of extremal oxidation states. The evaluation of the present state of valence theory depends on the field of chemistry. Several thousand molecular orbital calculations have been carried out for organic systems, slightly fewer for inorganic systems, and only about thirty for actinide

molecules. This is due to a number of factors, primarily the fact that the experimental data which are usually employed in theoretical calculations are not available for the actinides; many are highly radioactive and difficult to obtain. To this must be added the significant mathematical difficulties: the carbon atom has six electrons, whereas the curium atom has ninety six, and the quantum-chemical study of a system of sixteen carbon atoms involves less difficulty than the study of any curium molecule.

The use of computers has led to considerable progress in lanthanide and actinide valence theories. Overall, however, the progress resulting from the use of computers has been less than seemed likely in the nineteen-sixties, when calculations by the Roothaan method began to be carried out for the first time in the Soviet Union. The existence of computers and their availability make the ideological content of quantum-chemical calculations and their relation to experiment of primary importance, since computers only process ideas. The mathematical apparatus of quantum mechanics is most effective in those cases where the chemical model of the phenomenon is clarified in collaboration with experimentalists, and afterwards an apparatus is selected using a computer, calculator, or slide rule, adequate for the problem being posed and effective for its solution. When applied to the study of extremal oxidation states of the lanthanides and actinides, this approach means not only the use of up-to-date quantum-mechanical atomic and molecular orbital calculations but also the search for various correlations on the basis of the experimental results obtained.

The Soviet experimental school has accumulated a large amount of experience in the study of extremal oxidation states of the lanthanides and actinides: Cm(VI),[1] Md(I),[2] Pu(II),[3] Pu(VII),[4] Am(VII),[5] Np(VII),[6] and Tm(IV) [7] have been discovered. This makes it possible to raise the question of the quantum-chemical prediction of the existence of both higher and lower oxidation states of the lanthanides and actinides: univalent lanthanides and actinides, plutonium(VIII) and americium(VIII), oxidation states of 5+, 6+, and 7+ for curium, 5+ and 6+ for californium and berkelium, and 4+ for holmium, erbium, and thulium. The prediction of a given oxidation state is an important aspect of the problem. The study of the electronic structure and properties of the lanthanides and actinides in unusual oxidation states is a no less important and apparently more complex question, including a number of problems: the determination of redox potentials, ionic radii, the geometry of molecular systems, and the study of reaction mechanisms, energy structure, etc.

The present review is devoted to the theoretical study of new oxidation states of the lanthanides and actinides and the investigation of the regular features of their structure in relation to Mendeleev's periodic law.

II. STABILITY OF THE LOWER OXIDATION STATES OF THE *f*-ELEMENTS

1. Characteristics of the Univalent State

A number of experimental studies have been devoted to the attempt to obtain lanthanides or actinides in univalent or singly-charged states. Fong[8] studied the reduction of lathanides to the singly-charged state in crystalline lattices. In particular, the broad absorption band in the thermoluminescence spectra of γ-irradiated Sm^{2+}/KCl specimens has been assigned to the electronic transition $4f^6 6s^1 \cdot\cdot 4f^5 6s^2$, corresponding to the reduction of Sm^{2+} to the univalent state. Similar experiments were carried out[9] for Sm^{2+}/KCl and Eu^{2+}/KCl specimens; no evidence in support of the formation of Eu^+ was obtained. Subsequently, experiments were carried out[10] including the additional high-temperature treatment of Sm^{2+}/KCl and Eu^{2+}/KCl specimens in potassium vapour. This gave fundamentally new (at T = 4.2 K) absorption bands in the thermoluminescence spectra of these specimens, which were assigned to the univalent states Sm^+ and Eu^+. Fong's data on the preparation of univalent europium were confirmed in 1978.[11]

A series of unique studies in the synthesis of univalent lanthanides has been carried out.[12–15] The compounds LnX, where Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, and Lu; and X = Cl, Br, were synthesised. The compounds obtained have a layer structure, and are isostructural with ZrCl or ZrBr.[15] Zirconium chloride has the sodium chloride structure with alternating layers of Zr and Cl atoms parallel to the (001) face. The coordination polyhedron of the Ln atom is an antiprism of Ln_3–Cl_3 atoms.[15] A characteristic feature of the structure is the presence of a bond between the metal atoms, so that these compounds have the properties of two-dimensional metals.

Among actinide atoms, an attempt has been made to obtain mendelevium(I); the conclusion that mendelevium(I) exists was based on its ability to cocrystallise with potassium hexachloroplatinate.[2]

In all the experiments, the crystal lattice acts as an additional factor stabilising the univalent state (KCl or K_2PtCl_6); in the compounds prepared in the works cited,[12–15] the corresponding factor is the formation of Ln_6 metal clusters. The methods of high-temperature chemistry have detected the existence of many neutral molecules with the formula LnF.[16] These are unstable molecules, analogous to the univalent alkaline earth metal halides; they have similar dissociation energies, for example: E_d(CaF) = 125.5 kcal mole^{-1}, E_d(SmF) = 127 kcal mole^{-1}, E_d(SrF) = 129.5 kcal mole^{-1}, and E_d(NdF) = 130 kcal mole^{-1}. Stable compounds of the univalent lanthanides and actinides have not been obtained in solution or the gas phase.

Experiments on the study of solid specimens raise a number of important theoretical problems regarding the electronic structure of these elements in the univalent state, namely: 1) the nature of the electron configuration of the *f*-elements; 2) the stability of the lower oxidation states in the actinide series; 3) the analogy between the actinides in lower oxidation states and other elements of the periodic system.

The valence possibilities of an atom are determined by the number of unpaired electrons, unshared electron pairs, unfilled atomic orbitals (AO), and the energy of excitation from one electronic state to another. For most elements of the lanthanide and actinide series, the electron configuration of the ground state is $f^n s^2$, so that the univalent state is realised when one *s*-electron is involved in chemical bond formation, and the other remains localised, as in the univalent alkaline earth metal halides. In contrast to the elements of group II, however, in the singly-charged lanthanides and actinides there may be rearrangement of the electron configuration, stabilising this state: $M^+(f^n s) \rightarrow M^+(f^{n+1})$ or $M^+(f^n s) \rightarrow M^+(f^{n-1} s^2)$, where M = Ln, An. For the group II elements there is no "inner" atomic orbital which might have been involved in a stabilisation process.

It is of interest to compare the excitation energies E_1 of the transition $f^n s \rightarrow f^{n+1}$ for singly-charged lanthanides and actinides (Table 1). Using the Hartree–Fock Hamiltonian as the zeroth approximation and applying perturbation theory to the calculation of the correction to the kinetic energy operator and to take account of spin–orbit coupling, and also the Darwin correction, the present

authors calculated the excitation energies for the singly-charged lanthanides and actinides.[18,19] The data in Table 1 lead to the following conclusions.[23]

Table 1. Promotion energies of the transition $f^n s \rightarrow f^{n+1}$ for singly-charged actinide and lanthanide ions (kcal mole^{-1}).[18-22]

An$^+$	[20, 21]	[18, 19]	[22]	Ln$^+$	[20, 21]	[22]
Ac$^+$	81.00	—	109.8	La$^+$	118.00	118.29
Th$^+$	94.00	91.2	85.52	Ce$^+$	98.00	96.79
Pa$^+$	86.00	83.58	78.37	Pr$^+$	91.00	97.82
U$^+$	78.00	77.17	72.36	Nd$^+$	94.00	99.73
Np$^+$	63.00	54.29	50.91	Pm$^+$	74.00	79.71
Pu$^+$	40.00	29.28	27.46	Sm$^+$	52.00	52.63
Am$^+$	92.00	86.61	81.23	Eu$^+$	166.00	162.60
Cm$^+$	68.00	57.02	53.48	Gd$^+$	137.00	134.20
Bk$^+$	46.00	35.67	33.46	Tb$^+$	114.00	115.66
Cf$^+$	46.00	34.76	32.61	Dy$^+$	126.00	122.24
Es$^+$	49.00	35.06	32.89	Ho$^+$	132.00	130.02
Fm$^+$	40.00	17.08	16.02	Er$^+$	123.00	113.08
Md$^+$	17.00	8.23	7.72	Tm$^+$	97.00	87.83

Note. Numbers in square brackets denote references (Ed. of Translation).

1. The energies of excitation into the univalent state for the singly-charged actinide ions are lower than those of the corresponding lanthanide ions.
2. The energies of excitation into the univalent states are lower for the second half of the actinides than for the first half, with the exception of Pu^+, which also has a low excitation energy $f^6s \rightarrow f^7$.
3. For the second half of the actinides, with increase in the atomic number, the excitation energy decreases, and the lowest excitation energy is shown by Md, at which the f^{14} shell is filled.
4. Of the lanthanides, Sm^+ ($f^6s \rightarrow f^7$ transition) and Pm^+ have the lowest excitation energies.

In addition to the electron configuration $f^n s$, an atom may be univalent in the electron configurations $f^n d$ and $f^n p$. The energy E of excitation into these states, however, is much greater than that into the state $f^n s$, and $E(f^n p) > E(f^n d) > E(f^n s)$. For all singly-charged actinides, the values of $E(f^n p)$ are greater than $E(f^n s)$ by ~3 eV. For U^+, Np^+, and Pu^+, the energy of the $f^n d$ electron configuration is higher than that of $f^n s$ by 1.0–1.5 eV; for the other elements of the actinide series, this difference gradually increases, reaching 3 eV for Md. These data indicate that for the univalent actinides, bond formation involves chiefly the 7*s* orbital; the 6*d* orbitals may play a small part in bond formation in the middle of the series (for U, Np, and Pu), but the 7*p* orbitals remain excited for all the univalent actinides; the 5*f* orbitals, like the other valence configurations ($f^n ds^2$, $f^n s^2$, $f^n sd$, etc.), remain core orbitals, deeper than the *s* orbital. Thus in the electron configuration $f^n s$ for the singly-charged actinide ions An^+, it is more difficult to remove an electron from an *f* orbital than from the *s* orbital; the difference in the ionisation energies $I_f - I_s$ is 2.1 eV for Pu, 3.3 eV for Am, 0.6 eV for Cm, 1.4 eV for Bk, 2.4 eV for Cf, 2.5 eV for Es, 2.1 eV for Fm, and 3 eV for Md.[20-22]

A second way in which the univalent state is stabilised is associated with the transfer of an *f* electron to the *s* level, that is $f^n s \rightarrow f^{n-1} s^2$. With a low excitation energy, a filled s^2 electron shell is formed. The data in Table 2 show that the values of the excitation energies $E_2(f^n s \rightarrow f^{n-1} s^2)$ are low, except for samarium and europium. It may be assumed that in the previously synthesised[12-15] monohalides LnCl, Ln = La, Ce, Pr, Nd, Gd, Tb, Ho, Er, the second route to the stabilisation of the univalent state is followed. They therefore have a distorted CdI_2 or $Mg(OH)_2$ structure, in which the central atoms also have an unshared pair of s^2 electrons. At the same time, samarium and europium differ from the other lanthanides: univalent europium should be the analogue of the alkaline earth elements, but Sm^+ can be stabilised by the first mechanism.

Table 2. Excitation energies for Ln^+ and An^+.[21]

An	$10^{-3} E_2$, cm^{-1}	Ln	$10^{-3} E_2$, cm^{-1}	An	$10^{-3} E_2$, cm^{-1}	Ln	$10^{-3} E_2$, cm^{-1}
Ac	—28.20	La	—6.75	Cm	—2.09	Gd	3.44
Th	—17.50	Ce	5.52	Bk	5.00	Tb	5.50
Pa	—8.00	Pr	16.00	Cf	12.00	Dy	12.336
U	—4.66	Nd	17.50	Es	12.00	Ho	10.00
Np	2.00	Pm	17.00	Fm	9.00	Er	7.00
Pu	8.19	Sm	24.00	Md	17.00	Tm	12.50
Am	18.50	Eu	33.00				

The univalent state in solution is characterised by the oxidation potential of the reaction

$$An^+_{aq}(f^{n+1}) \rightarrow An^{2+}_{aq}(f^n) + e$$

or

$$An^+_{aq}(f^{n-1}s^2) \rightarrow An^{2+}_{aq}(f^{n-1}s^1) + e$$

The factors determining the stability of the univalent state can be considered. The energy balance of the reaction is determined by the difference between the ionisation energy of the actinide ion in the univalent configuration and the energy of excitation from the univalent to the bivalent state $\varepsilon_1 = I - E_1$, and also by the difference in the free energies of hydration for these oxidation states, δF_n.

Table 3. Ionisation energies of singly-charged lanthanide and actinide ions in the electron configuration $f^{n-1}s^2$.[24,25]

Configuration	Term	Ln	$10^{-3} I'$, cm^{-1}	An	$10^{-3} I'$, cm^{-1}
f^0s^2	^1S	La	17.5	Ac	18.0
f^1s^2	^1F	Ce	33.8	Th	27.9
f^2s^2	^3H	Pr	47.9	Pa	47.2
f^3s^2	^4I	Nd	45.7	U	59.0
f^4s^2	^5I	Pm	44.6	Np	66.5
f^5s^2	^6H	Sm	55.5	Pu	101.4
f^6s^2	^7F	Eu	68.9	Am	88.0
f^7s^2	^8S	Gd	7.9	Cm	59.3
f^8s^2	^7F	Tb	24.4	Bk	91.7
f^9s^2	^6H	Dy	34.7	Cf	108.0
$f^{10}s^2$	^5I	Ho	32.5	Es	118.7
$f^{11}s^2$	^4I	Er	27.4	Fm	136.7

Factors increasing the stability of the univalent state are a high value of the ionisation energy of the singly-charged ion and a low excitation energy. From data on the ionisation energies of $An^+(f^n s)$, calculated in the relativistic Hartree–Fock approximation,[19] and from the excitation energies E_1 (Table 1), it follows that in the second half of the actinide

series, the most stable univalent state, corresponding to the minimum value of E_1, is shown by mendelevium. For univalent states stabilised by the second mechanism with the production of the electron configuration $f^{n-1}s^2$, the stability of the univalent state to oxidation is also determined by the quantity $\varepsilon_2 = I' - E_2$, where the corresponding values relate to the electron configuration $f^{n-1}s^2$. Table 3 gives the values of the ionisation energies for the electron configuration $f^{n-1}s^2$.[24,25] Comparison of the values of E_2 and I' shows that: 1) in the lanthanide series, the stability of the univalent state in solution with respect to oxidation is low; 2) in the actinide series, the stability of the univalent state in solution is higher than for the corresponding lanthanides.

2. Ionic Radii

The determination of the ionic radii of the actinides in lower oxidation states is important for establishing the similarity in the properties of the actinide elements and the elements of other groups of Mendeleev's periodic system. The solution of this problem is difficult, because of high radioactivity and the difficulty of obtaining the heavy actinides. At present, californium is apparently the last element for which ionic radii can be calculated from structural data. There are extremely few published data on the ionic radii of the actinides in lower oxidation states. Of the bivalent actinide compounds, americium di-iodide has been prepared; the measured interatomic distance in this compound, $R_{Am-I} = 3.28-3.40$ Å, indicates that the ionic radius of americium is 1.12–1.24 Å.[26]

Comparison of the lattice parameters of AmI_2 and EuI_2 [27] indicated that $R_{Am^{2+}} = 1.1$ Å, $R_{Eu^{2+}} = 1.09$ Å, and comparison of the lattice parameters of $EuBr_2$, $CfBr_2$, and $SrBr_2$ showed that $R_{Cf^{2+}} = 1.08$ Å. The similarity in the crystallisation coefficients of Sr^{2+} and Fm^{2+} with $SmCl_2$ indicates that the ionic radii of these elements differ by not more than 5%. Finally, comparison of the behaviour of Sr, Ca, and No in extraction and ion-exchange systems[28] indicated that the ionic radius of nobelium(II) lies in the range of the ionic radii of strontium and calcium.

Quantum-chemical methods make it possible to calculate the distance from the nucleus to that part of the ion where there is the maximum electron density R_{max}. Slater[30] has shown that the value of R_{max} for singly-charged ions is related to the crystal ionic radius by the simple relationship $R_{cr} = c_n R_{max}$, where c_n is a coefficient which depends on the principal quantum number n of the outer valence shell of the ion. For the f-elements of a given series, existing in the same charge state and therefore having the same valence f-orbital, the value of c_n apparently remains constant for the elements of the entire series. The Slater functions are crude approximations for the f-elements; better agreement can be obtained using the Hartree–Fock radii of the maximum electron density, calculated in the relativistic approximation.[24,25]

The Hartree–Fock values of R_{max} for the lanthanides and the crystal ionic radii of these elements in the tervalent state have been used[29] to calculate the coefficients c_n, which were found to be constant for all elements of the 4f series ($c_n = 1.257$). Similarly, the coefficients remain constant for the tervalent actinides from plutonium to einsteinium ($c = 1.21$). Pauling's relationship for isoelectronic ions[31] has been used to calculate the ionic radii for univalent and bivalent actinides;[30] the following values were obtained for the ionic radii of the doubly-charged actinide ions (Å):

Am^{2+}	Cm^{2+}	Bk^{2+}	Cf^{2+}	Es^{2+}	Fm^{2+}	Md^{2+}	No^{2+}
1.17	1.16	1.14	1.06	1.05	1.05	1.04	1.02

The ionic radii of the doubly-charged actinides calculated in this way agree with available experimental data. Thus the value of $R_{No^{2+}}$ lies in the range between the ionic radii of strontium and calcium.[32] The ionic radius of Fm^{2+} is close to the ionic radii of Sr^{2+} and Sm^{2+}; the ionic radius of Cf^{2+} agrees with the experimental data, which show that CfI_2 and CdI_2 are isostructural, and is close to the suggested[27] value of 1.08 Å.

The value obtained for the ionic radius of Am^{2+} shows good agreement with the experimental internuclear distance R_{Am-I} in AmI_2. Published data[27] on the ionic radius of americium, $R_{Am^{2+}} = 1.1$ Å, do not agree with the Hartree–Fock calculations, since the proportional relationship between $R_{max}(Am^{2+})$ and $R_{cr}(Am^{2+})$ breaks down. The value 1.21 Å was obtained[30] for $R_{cr}(Md^{+})$; the ionic radius of Md^{+} calculated in this way is close to that of Ag^{+} (1.13–1.26 Å).

III. HIGHER OXIDATION STATES OF THE LANTHANIDES AND ACTINIDES

1. Relationship Between the Oxidation Potentials and the Electronic Structure of the Central Atom

The marked increase in interest in compounds of the f-elements in unusual oxidation states can be attributed to two factors. Firstly, the discovery of nuclear decay and the subsequent development of nuclear energy have led to the detailed study of the chemistry of the lanthanides, the principal fission products found in the nuclear reactor, and of the chemistry of the transuranium elements, which are also formed at the same time. Secondly, there has been an increase in the role of the lanthanides and actinides in industry and a consequent increase in the need to study their properties and predict nontrivial oxidation states.[34]

It has been suggested[33] that einsteinium(IV) should exist in compounds with the fluorite structure. French workers, using thermochromatography, were the first to prove the existence of einsteinium(IV) fluorides,[35] and also curium(V) and (VI).[138] The behaviour of EsF_4 in the gas phase is analogous to that of CmF_4, BkF_4, and CfF_4.

It has been suggested that einsteinium(IV), fermium(IV) and mendelevium(IV) can exist as the double salts $Li_3.AnF_7$,[36] and berkelium(V), californium(V), and einsteinium(V) as the oxygen compounds Li_7AnO_6.[34] It has also been suggested that einsteinium(VI) and fermium(VI) can be obtained as the hexafluorides.[37] These suggestions, which undoubtedly contain elements of new ideas, have not been confirmed by calculations, estimations, or other evidence.

French workers,[38] on the basis of a calculation of the thermodynamic characteristics of the 5f elements, estimated the stability of berkelium(V) and californium(V), and showed that Cf(V) should be stable, and Bk(V) unstable, in aqueous solutions. The stability of a given oxidation state is determined by the oxidation potential of the reaction $An^{z+}(m) \rightarrow An^{z'+}(m+1) + e$, which in turn is determined by all the changes taking place when the central ion with effective charge z and oxidation number m is converted into a state with oxidation state $m+1$ and charge z'. The free

energy change F in the oxidation, $F = \pm\varepsilon + I + \Delta F_h$, includes the ionisation energy I, the energy $\pm\varepsilon$ used in the rearrangement of the electron configuration of the ion An^{z+} in the change from the state with oxidation number m to the state with oxidation number $m + 1$, and ΔF_h is the change in the free energy of hydration.

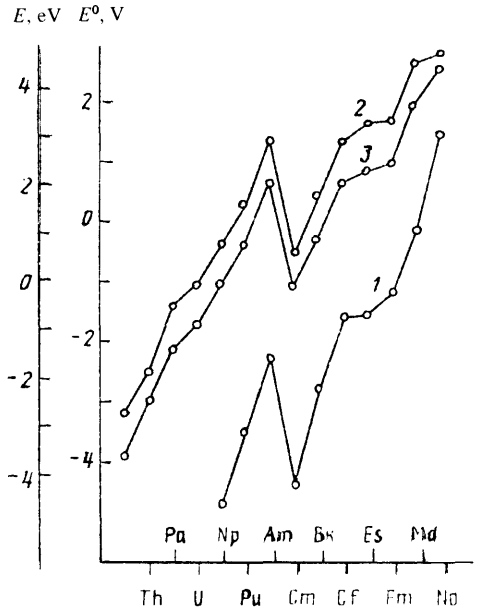


Figure 1. Dependence of the oxidation potentials E^0(II–III) (*1*) and the excitation energies $E = \varepsilon(f^n) - \varepsilon(f^{n-1}d)$ (*2*) and $E = \varepsilon(f^n s^2) - \varepsilon(f^{n-1}ds^2)$ (*3*) on the atomic number of the element.[107]

Within the framework of the covalent model, the electron configurations of the bivalent state $f^n s^2$ and the tervalent state $f^{n-1}ds^2$ in the approximation of the ionic model are f^n and $f^{n-1}d$ respectively. In both approximations, the value of ε changes in the same sense as the potentials E^0(II–III).[57] Fig. 1 gives the dependence on the atomic number of the elements of the oxidation potentials E^0(II–III) and the excitation energy, calculated for the two electron configurations from published data.[20–22] The main regular features of the dependence of other oxidation potentials on the atomic number of the element are also determined by the energy used up in the rearrangement of the electron levels of the actinide atoms or ions.[57,59] Change in the heats of hydration leads to renormalisation of the oxidation potentials, without changing their course. The linear relationship between the oxidation potentials and the energy of excitation of an f-electron into the d-level (Figs. 2 and 3) makes it possible, from the correlation rules alone, to judge whether a transition into the next oxidation state takes place. In this connection, an important role is acquired by calculations of the energy of the f- and d-levels in actinide and lanthanide atoms and ions.

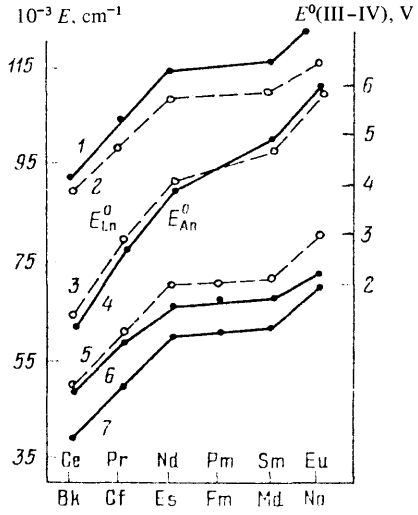


Figure 2. Change in the same sense in the oxidation potentials E^0(III–IV): *3*) Ln, *4*) An, and excitation energies for triply-charged lanthanide and actinide ions:[107] *1*) $An(f^n \to f^{n-1}p)$, *2*) $Ln(f^n \to f^{n-1}s)$, *5*) $Ln(f^n \to f^{n-1}d)$, *6*) $An(f^n \to f^{n-1}s)$, *7*) $An(f^n \to f^{n-1}d)$.

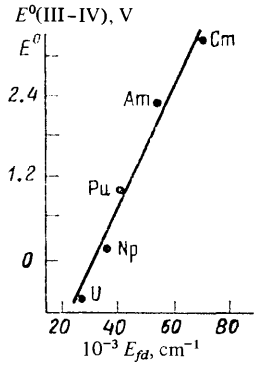


Figure 3. Linear relationship between the oxidation potentials E^0(III–IV) and the excitation energy.[107]

2. The Approximation Based on Calculations for Free Atoms and Ions

Atomic calculations give the first representations of the energy levels of atoms, and characterise the radial wavefunctions. These calculations can be used to reach important chemical conclusions about the possible oxidation states of atoms, the regular features of the change in stability, the specific features of the behaviour of the

actinide ions in solids, etc. Although calculations for molecules are used to reach definite chemical conclusions, calculations for atoms and ions are rarely used to interpret chemical data. These calculations may be useful, however, for an understanding of qualitative chemical regularities.

Atomic calculations for the actinides have an extensive history. Herman and Skillman[39] found solutions of the Hartree–Fock–Slater equation for all atoms up to element 103. Almost simultaneously,[40] the Hartree equation was solved with an exchange correction to the total energy. The first relativistic calculations for atoms, including uranium, were carried out[41] without allowance for exchange. Subsequently,[42] relativistic calculations were carried out with allowance for exchange by Slater's method, and account was taken of the effect of the finite dimensions of the nuclei.[43] Unfortunately, these calculations do not always correlate with the chemical properties. In Ref. 43, for berkelium and fermium, the electron configurations f^8ds^2 and $f^{11}ds^2$, corresponding to a more stable tervalent state, were obtained, whereas in fact they are more stable in the bivalent state. The difference in the energies of the 5*f*-orbitals of californium and einsteinium should not be so large as found in Ref. 43, since the oxidation potentials E^0(II–III) for these elements are similar.[44]

The use of the Slater exchange potential for large radii is an approximation, since the potential tends to zero according to an exponential law, and not as r^{-1}. The use of different coefficients[45–47] in the exchange potential improves the results, although the crude asymptotic form of the approximation is preserved. A number of authors have studied the question of why the local approximation is crude for large radii.[48–50] In Ref. 51, a first-order correction was introduced into the local approximation, using as the functions of the zeroth approximation the functions obtained in Ref. 52. The results[51] also show some lack of agreement with experiment. For the plutonium atom, the calculated energy of the 5*f* orbital is higher than that of the 7*s* orbital, whereas the opposite relationship should be observed. The energy parameters obtained[51] for americium indicate a very low ionisation energy (2.885 eV), and also show that it should be stable in the univalent or tervalent states, but not in the bivalent state; the energy parameters of berkelium correspond to stable tervalent and quinquevalent states. None of this agrees with experiment. Moreover, for Cf, the difference between the energy of the 5*f* and 7*s* orbitals is so small that its electron configuration should lead to a stable sexavalent state, which again does not agree with experiment. Beginning from einsteinium, however, adequate qualitative agreement between the calculated and experimental parameters is observed.

Hartree–Fock calculations of the electronic structure of atoms have been carried out by Mann.[53] Although these were non-relativistic calculations, exchange terms were taken into account without approximation; it was found that the 7*s* orbital (6*d* orbital in Refs. 43 and 51) is responsible for the ionisation energy. Although the values of the energy of the 6*d* orbitals obtained by Mann[53] are slightly low, the energies of the 5*f* orbitals give qualitatively the regular chemical features relating to the stability of the bivalent and tervalent states of the actinides. The absolute values of the energies of the 5*f* orbitals obtained in Ref. 53 differ by a factor of 2–2.5 from those obtained in Refs. 43, 51, and 54. In Ref. 53, these energies are systematically too low, possibly due to the neglect of relativistic effects.

In a series of calculations by Desclaux, the Dirac–Fock equation was solved without approximations for the exchange terms; the nuclei were regarded as spheres with uniform charge distribution,[54] in accordance with the published procedure.[55,56] A noteworthy feature is the small difference in the orbital energies of the 6*d* and 7*s* levels, which explains many experimental facts. In the thorium atom, the 6*d* orbital is deeper than the 7*s* orbital, that is thorium is an analogue of the transition elements; for protactinium, uranium, neptunium, and curium, on the other hand, the 7*s* orbital is lower than the 6*d* orbital, and this explains the stabilisation of the electron configuration f^ns of their singly-charged ions.[54]

In the first half of the series, the energies of the valence 5*f* orbitals differ little from the energies of the 6*d* and 7*s* orbitals, indicating that the elements of the first half of the series tend to form higher oxidation states. In the second half of the series, this difference gradually increases, again in agreement with the experimentally observed stabilisation of the bivalent state in the second half of the actinide series. The absolute values of the energies of the 5*f* orbitals explain their participation in chemical bond formation and the sequence in the arrangement of the molecular orbitals in actinide molecules and complexes.

Thus many atomic calculations give correctly the regular features of the electronic structure of the lower oxidation states of the actinides An(II) and An(III), and this gives grounds for using these calculations for the higher oxidation states also. The present authors carried out a series of calculations for the atoms of the 5*f* elements in excited configurations with the participation of the 6*d* orbitals and positively charged ions by the Hartree–Fock method with allowance for relativistic corrections.[61] According to these calculations, carried out for actinide ions in the electron configuration f^n,[19] the energy of removal of the last *f*-electron (Ry) increases sharply on going from Ac to Pu:

Ac	Th	U	Np	Pu
1.53068	2.70432	5.43696	6.97975	8.63445

The correlation of these ionisation energies with the known oxidation potentials corresponding to the change to higher oxidation states leads to a high potential for plutonium: E^0(VII–VIII) ≅ 4 V.

When applied to the change to a higher oxidation state, it may be assumed that the relative depth of the potential well for the $5f^1$ electron configuration is determined by the energy of splitting of the ^2F term as a result of spin–orbit coupling. Using the calculated[19] spin–orbit coupling constants for the actinides in the f^1 electron configuration from the actinium atom to the americium atom (cm^{-1})

Ac	Th	Pa	U	Np	Pu	Am
707	960	1211	1472	1747	2038	2337

for correlation with the known potentials also gave a high oxidation potential for plutonium: E^0(VII–VIII) ≅ 4 V; the oxidation potential obtained for the americium couple was even higher: E^0(VIII–IX) ≅ 5.8 V.

An important factor in the comparative estimation of the stability of f^n electron configurations with $n > 1$ is the interelectronic interaction, determined by the Racah parameters E^0, E^1, E^2, E^3. The ionisation energy[62] of an *f*-element in the electron configuration f^n can be expressed in terms of the Racah parameters and *W*, the Coulomb energy in the field of the positively charged core, imitating the cloud of the inert gas radon (Table 4).

The change in the energy of the electrostatic interaction with change in the number of electrons determines the binding energy of the valence electrons with the core. For example, exchange interaction increases the ionisation energy in the electron configuration f^{10} by $+12E^3$, makes no contribution to the electron configuration f^{11}, and decreases the ionisation energy in the electron configuration f^{12} by

$-12E^3$. The parameter W also changes with change in the number of electrons, but these changes are not so great for the lanthanides as for the actinides; thus for the 4*f*-elements, the parameter E^3 can influence the relative stability of a given oxidation state along the series. The stabilities of the 4+ oxidation states of the lanthanides show interesting regular features. From the experimental values of the oxidation potentials E^0(III–IV), it follows[58,75] that the stability of the 4+ oxidation state decreases on going from cerium to neodymium in the first half of the series and from terbium to dysprosium in the second. In other words, the stability of the 4+ oxidation state decreases towards the end of the series.

Table 4. Ionisation energy of actinides with the electron configuration f^n.[62]

n	$I=E(f^{n-1})-E(f^n)$	n	$I=E(f^{n-1})-E(f^n)$
1	W	8	$W-7E^0-9E^1$
2	$W-E^0+9E^3$	9	$W-8E^0-9E^1+9E^3$
3	$W-2E^0+12E^3$	10	$W-9E^0-9E^1+12E^3$
4	$W-3E^0$	11	$W-10E^0-9E^1$
5	$W-4E^0-12E^3$	12	$W-11E^0-9E^1-12E^3$
6	$W-5E^0-9E^3$	13	$W-12E^0-9E^1-9E^3$
7	$W-6E^0$	14	$W-13E^0-9E^1$

When the change in the parameter E^3 for the electron configurations f^{10}, f^{11}, and f^{12}, corresponding to triply-charged holmium, erbium, and thulium, is taken into account, the opposite trend in the stabilities of the 4+ oxidation state can be expected for these elements: Ho < Er < Tm. This is confirmed by the fact that for holmium, erbium, and thulium, there is a decrease in the energies of excitation from the f^n (n = 10, 11, 12) to the $f^{n-1}d$, $f^{n-1}p$, and $f^{n-1}s$ states.[19] For the actinides, there is a gradual increase in the corresponding energies from californium to nobelium (Fig. 4). These facts indicate that the stability of the 4+ oxidation state increases towards the end of the lanthanide series from holmium to thulium, and decreases towards the end of the actinide series from einsteinium to nobelium, that is in the actinide series on going from Es to No, the most stable 4+ oxidation state is shown by einsteinium, whereas in the lanthanide series it is shown by thulium. The preparation of compounds of thulium(IV)[7] and einsteinium(IV),[35] Cs_3TmF_7 and EsF_4, confirmed these theoretical predictions.

The sharp increase in the ionisation energy for the half-filled f^7 electron configuration compared with the f^8 configuration is due to the appearance of the term $-9E^1$ for n = 8. When applied to Cm, this means that it gives up an electron with greater difficulty in the tervalent state than in the quadrivalent state, but in the quinquevalent state the binding of the remaining five electrons to the core is decreased as a result of electrostatic repulsion, so that Cm(V) should be more readily converted into Cm(VI), compared with the conversion of Cm(IV) into Cm(V). Finally, Cm(VI) and Cm(III) are analogues in the sense that the interelectronic interaction parameter E^3 does not make a contribution to the binding energy of the remaining electrons to the core. Thus the potential E^0(VI–VII) for Cm should be high, like E^0(III–IV). Even this qualitative approach determines the chemical properties. For a quantitative estimate of the oxidation potentials, the correlation with the energies of the *fd*-transitions can be used.[64–68]

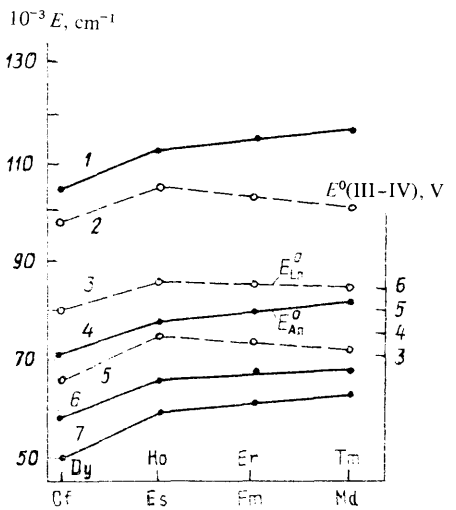


Figure 4. Change in the opposite sense in the oxidation potentials E^0(III–IV): *3*) Ln, *4*) An, and the excitation energies for triply-charged actinides and the corresponding lanthanides:[107] *1*) An($f^n \rightarrow f^{n-1}p$), *2*) Ln($f^n \rightarrow f^{n-1}s$), *5*) Ln($f^n \rightarrow f^{n-1}d$), *6*) An($f^n \rightarrow f^{n-1}s$), *7*) An($f^n \rightarrow f^{n-1}d$).

Published data on the transition energies have been obtained from the atomic spectra and the spectra of multiply ionised ions,[20,21,69,70] from thermochemical data for metals,[20,21] the electronic spectra of compounds,[71,72] the spectra of actinide ions in matrices, from Hartree–Fock calculations for free atoms and ions with allowance for relativistic corrections,[39–43,45–47,51–56] and finally by linearisation of the parameters of Coulombic and spin–orbit interactions.[22] The absolute magnitudes of these quantities do not always coincide, due chiefly to the marked broadening of the bands in the spectra as a result of spin–orbit coupling. Thus for uranium with a charge of 5+ in the electron configuration f^1, the terms of the ground state ^2F and the first excited state ^2D are split by spin–orbit coupling $^2F \rightarrow {}^2F_{5/2} + {}^2F_{7/2}$, $^2D \rightarrow {}^2D_{3/2} + {}^2D_{5/2}$ by 7609 cm^{-1} and 9511 cm^{-1}.[69] In accordance with the increase in the atomic number, the splitting energy of the ^2F term for Np^{6+} and Pu^{7+} increases. There is an analogous increase in the splitting energy of the ^2D term.[69] Thus for the transuranium elements it is possible to speak only of a qualitative charge dependence of the energy of the *fd* transition. On the basis of available experimental data on the energies of *fd* transitions, the present authors calculated the difference in the energies of the f^n and $f^{n-1}d$ states for the multiply ionised ions from actinium to curium; the data obtained are given in Table 5.[19,63,68] The correlation of the values of E_{fd} obtained with the known oxidation potentials indicates that curium(VI) is stable in solution: E^0(V–VI) = 5.1 V, whereas E^0(IV–V) = 1.7 V and E^0(VI–VII) = 2.7 V. The preparation of curium(VI)[1] confirmed these theoretical predictions. This approach indicated that californium(V)

is stable,[73] as confirmed experimentally,[74] and also that einsteinium(VI) is stable, E^0(V–VI) = 1.5 V. According to these estimates, berkelium(V) and californium(VI) should be unstable in solution.

Table 5. Excitation energies from the f^n electron configuration to $f^{n-1}d$ (10^{-3} E_{fd}, cm^{-1}).[63]

n	Ac	Th	Pa	U	Np	Pu	Am	Cm
1	—20.0	5.0	31.0	57.5	82.5	—	—	—
2	—	—15.1	17.5	52.5	87.5	120.0	—	—
3	—	—	—5.0	27.0	55.0	82.5	112.5	—
4	—	—	—	0.5	35.0	70.0	104.0	—
5	—	—	—	—21.0	9.1	40.0	70.0	100.0
6	—	—	—	—	—12.5	17.5	51.0	82.5
7	—	—	—	—	—	—5.0	24.0	57.5

3. Molecular-Orbital Analysis of Octahedral Complexes

Since the discovery of septavalent neptunium, plutonium, and americium,[4–6] a large amount of experimental material has accumulated,[76] and the problems still to be solved have become clear. These problems are related primarily to the study of the electronic structure of compounds of neptunium(VII), plutonium(VII), and americium(VII), and cover a wide range of questions: the electron density distribution, the structure of the energy levels, the regular features of the change in the ionisation energies and electron affinity, the determination of the oxidation potentials, and the interpretation of the electronic spectra. The discovery of the highest oxidation state of neptunium raised the question of the possible existence of plutonium(VIII), which can be resolved only by a systematic study of the high oxidation states of uranium, neptunium, plutonium, and americium.

To resolve these problems, Pershina[77,78,95] carried out a a series of molecular orbital calculations for octahedral oxyanions UO_6^{7-}, UO_6^{6-}; NpO_6^{7-}, NpO_6^{6-}, NpO_6^{5-}; PuO_6^{6-}, PuO_6^{5-}, PuO_6^{4-}; AmO_6^{6-}, AmO_6^{5-} [77–80] by the semi-empirical molecular orbital method[81] using numerical Hartree–Fock functions.[53] The choice of objects of study is not accidental: most compounds of the actinides in the highest oxidation states in solution, and also those obtained by solid-phase synthesis, are oxygen compounds.

It follows from molecular orbital calculations that the effective charges on the central atoms do not exceed 2+ (Table 6). For isoelectronic anions they decrease with increase in the atomic number of the central atom. Table 6 shows that the populations of the 5*f* orbitals differ considerably from those given by crystal field theory. The population of the 6*d* orbitals corresponds to approximately two electrons. This is an interesting fact, since the ground state of the neutral atoms does not contain more than one 6*d* electron. With increase in the oxidation state of the actinide, the population of the 6*d* orbital increases; at the same time the population of the 5*f* orbital decreases, that is the oxidation is accompanied by the excitation of an electron into the 6*d* level. The population of the 7*s* orbital is low, and changes little from one compound to another.

A typical energy level diagram for octahedral oxyanions is shown in Fig. 5 for the UO_6^{7-} ion. The low-lying energy levels correspond to the interaction of the 2*s* and 2*p*σ orbitals of the oxygen atoms and the 7*s*, 6*d*, and 5*f* orbitals of the actinide atom. These are predominantly ligand orbitals. The next group of levels corresponds to pure σ or mixed (σ–π) molecular orbitals. In all the anions studied, the system of bonding levels is completed by quasi-degenerate molecular orbitals (MO), corresponding to oxygen atomic orbitals (AO), which are separated from the antibonding MO by an energy gap of width Δ*E*. For the diamagnetic ions UO_6^{6-}, NpO_6^{5-}, and PuO_6^{4-}, the values of Δ*E* are low, indicating the possible existence of polarisation temperature-independent paramagnetism.

Table 6. Populations of the *s*-, *d*-, and *f*-orbitals (*e*).[77,78]

Orbital	U(V)	U(VI)	Np(VI)	Np(VII)	Pu(VI)	Pu(VII)	Pu(VIII)	Am(VI)	Am (VII)
s	0.29	0.28	0.28	0.26	0.27	0.25	0.23	0.26	0.25
d	2.10	2.30	2.21	2.34	2.10	2.25	2.40	2.08	2.21
f	1.75	1.47	2.80	2.70	4.04	3.92	3.84	5.19	5.11

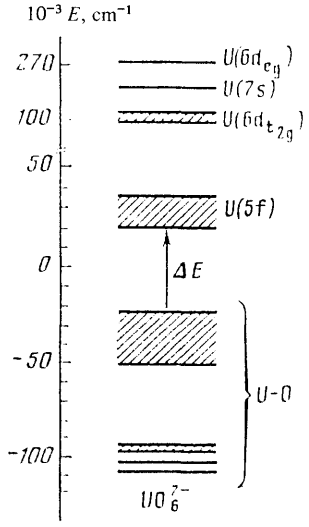


Figure 5. Typical energy level diagram for octahedral oxyanions of the actinides: the uranium(V) oxyanion.[107]

In the isoelectric ions, the magnitude of the crystal field splitting increases from U(VI) to Np(VII) and Pu(VIII) (Fig. 6). The magnitude of the splitting increases with increase in the oxidation state of the central ion; for example, for PuO_6^{6-}, PuO_6^{5-}, and PuO_6^{4-}, the magnitude of the splitting is 18030, 23260, and 28080 cm^{-1} respectively.[77–80]

In the highest oxidation states, the ionisation potential is determined by the molecular orbital t_{1u}. The energy of this MO decreases on going from U(VI) to Np(VII) and Pu(VIII) in accordance with the decrease in the effective negative charge on the ligands. As a result of the stabilisation of the 5*f* orbitals of the actinide atoms with increase in the atomic number in the isoelectronic anions,

the energy of the non-bonding $2\Gamma_7^-$ level decreases in the order U(VI) > Np(VII) > Pu(VIII), so that the electron affinity for PuO_6^{5-} is ~5.8 eV. This is apparently one of the main reasons for the instability of plutonium(VIII) in the oxyanion form. In anions with the $(2\Gamma^-)^1$ configuration, this level is also stabilised with increase in the atomic number of the actinide; thus U(V) is readily converted into U(VI), whereas plutonium(VII) is not oxidised.

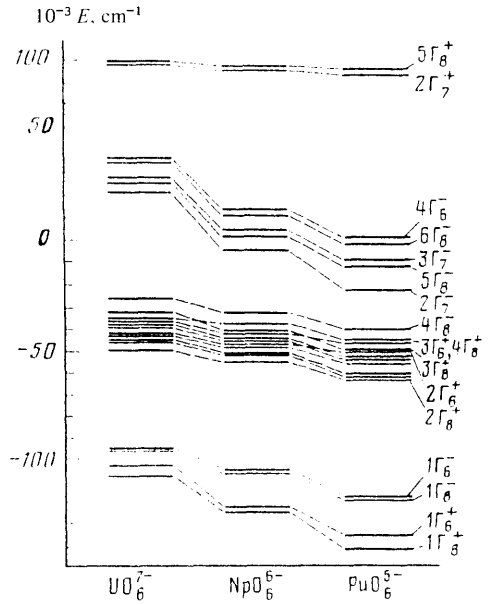


Figure 6. Change in the energy levels in isoelectronic oxyanions with increase in the atomic number of the actinide.[107]

Usually, three groups of bands are interpreted in the electronic spectra of actinide compounds: *ff*, *fd*, and charge-transfer transitions. This interpretation has been carried out in detail for uranium, neptunium, and plutonium hexahalides,[82-88] for actinyl ions,[89] and for a number of complexes.[90-93] The *ff* transitions in various octahedral oxyanions have been assigned.[94] A complete analysis of the electronic spectra on the basis of molecular orbital calculations for the entire series of octahedral oxyanions from U to Am has not been carried out. In the diamagnetic anions of U(VI), Np(VII), and Pu(VIII), the lowest transitions take place from the molecular orbitals $3\Gamma_6^+$ and $4\Gamma_8^+$ into antibonding MO with symmetry Γ_7^- and Γ_8^-. This leads to the existence of seven charge-transfer transitions allowed by the dipole selection rules (Table 7). Seven fine-structure bands appear in the absorption spectrum. This absorption band is displaced towards longer wavelengths in the series U(VI) → Np(VII) → Pu(VIII).

Additional absorption bands may also appear in the spectrum, since many of the MO are practically non-bonding. Two such additional bands are formed by transitions from the orbitals $2\Gamma_6^+$, $3\Gamma_8^+$ and $1\Gamma_6^+$, $2\Gamma_8^+$ (Table 7).

Table 7. Energies of the charge-transfer bands (10^{-3} *E*, cm^{-1}).[78]

Transition	UO_6^{6-}	NpO_6^{5-}	PuO_6^{4-}
$3\Gamma_8^+ \rightarrow 5\Gamma_8^-$	45.6	32.3	26.6
$3\Gamma_6^+ \rightarrow 6\Gamma_8^-$	57.7	45.2	39.8
$4\Gamma_8^+ \rightarrow 2\Gamma_7^-$	40.2	25.1	15.6
$4\Gamma_8^+ \rightarrow 5\Gamma_8^-$	45.6	32.3	26.6
$4\Gamma_8^+ \rightarrow 3\Gamma_7^-$	51.2	35.6	31.4
$4\Gamma_8^+ \rightarrow 6\Gamma_8^-$	57.7	45.2	39.8
$4\Gamma_8^+ \rightarrow 4\Gamma_6^-$	58.2	46.2	43.7
$2\Gamma_6^+ \rightarrow 5\Gamma_8^-$	51.9	38.2	32.0
$2\Gamma_6^+ \rightarrow 6\Gamma_8^-$	64.0	51.1	45.2
$3\Gamma_8^+ \rightarrow 2\Gamma_7^-$	42.1	30.3	23.5
$3\Gamma_8^+ \rightarrow 5\Gamma_8^-$	47.6	37.6	34.5
$3\Gamma_8^+ \rightarrow 3\Gamma_7^-$	53.1	40.8	39.3
$3\Gamma_8^+ \rightarrow 6\Gamma_8^-$	59.4	50.5	47.7
$3\Gamma_8^+ \rightarrow 4\Gamma_6^-$	60.2	51.4	51.6
$2\Gamma_8^+ \rightarrow 2\Gamma_7^-$	56.2	41.9	33.0
$2\Gamma_8^+ \rightarrow 5\Gamma_8^-$	61.6	49.2	43.9
$2\Gamma_8^+ \rightarrow 3\Gamma_7^-$	67.2	52.5	48.8
$2\Gamma_8^+ \rightarrow 6\Gamma_8^-$	73.7	62.1	57.2
$2\Gamma_8^+ \rightarrow 4\Gamma_6^-$	74.2	63.1	61.0

Extensive experimental material has been published[76] on the electronic absorption spectra of actinides(VII) (Pu, Am) in alkaline solutions. The regular features in the spectra, corresponding to charge-transfer bands, are the same as for the highest oxidation states. Fine structure of the main band is observed, apparently as a consequence of spin–orbit coupling of the energy levels in the complex, particularly the levels with a large contribution from the 5*f* orbitals of the atoms. For systems with the $5f^1$ electron configuration of the actinide (UO_6^{7-}, NpO_6^{6-}, PuO_6^{5-}), transitions of the *ff* type appear, with calculated energies lying in the ranges 4170–14340, 5944–17020, and 9070 to 22040 cm^{-1} respectively.[77,78] The energies of the *fd* transitions in these complexes and the experimental values of the oxidation potentials E^0(V–VI) for uranium and E^0(VI–VII) for neptunium[76] make it possible to estimate the oxidation potential for plutonium: E^0(VII–VIII) = 3.7 V. This confirms the conclusion, based on atomic calculations, that plutonium(VIII) is unstable in solution.[78]

A similar analysis of the electronic structure and properties has been carried out for the octahedral chloro-anions of actinides(III) and (IV) $AnCl_6^{z-}$.[95,96] In the An(IV) complexes, the populations of the 6*d* orbitals decrease with increase in the atomic number of the element, smoothly on going from Pa to Np and then more sharply on going to Pu, and the populations of the 5*f* orbitals increase in the same direction. The energies of the charge-transfer transitions pass through an extremal value for curium (Table 8). The calculations of the energies of the *ff* transitions give good agreement with experiment (Table 9);

this makes it possible to use the calculated values of the energy for those complexes for which there are no experimental data. The energies of the *fd* transitions and their correlation with known oxidation potentials have been used to determine the oxidation potential E^0(IV–V) for californium, which indicated that californium(V) is stable.[80]

Table 8. Energies of the charge-transfer bands (10^{-3} E, cm^{-1}) for octahedral chloro-complexes $AnCl_6^{2-}$.

An	Pa	U	Np	Pu	Am	Cm	Cf
Theory (Ref.131)	46.07	38.70	34.30	28.00	22.60	12.60	22.10
Experiment (Ref.97)	—	39.00	33.10	27.90	—	—	—

Table 9. Energy of the *ff* electronic transitions (10^{-3} E, cm^{-1}).

$\Gamma_\mu - \Gamma_\nu$	Complex	$\Gamma_7 - \Gamma_8$	$\Gamma_7 - \Gamma_8'$	$\Gamma_7 - \Gamma_7'$
Theory (Ref.131)	$PaCl_6^{2-}$	8.410	7.260	5.650
Experiment (Ref.97)	$(NEt_4)_2PaCl_6$	8.011	7.022	5.330

4. Cationic Forms of the Highest Oxidation States of Uranium, Neptunium, and Plutonium

Since plutonium(VIII) is unstable as PuO_6^{4-},[107] the question of its possible existence as molecules or cations arises. The PuO_4 molecule with tetrahedral or square coordination of the ligands should have an even greater electron affinity than the oxyanion. The cationic form of high oxidation states of neptunium and plutonium, in particular NpO_2^{2+} and PuO_2^{3+}, have been regarded as realistic by a number of authors,[97] so that the existence of PuO_2^{4+} might also be assumed.

The change in the stability of the isoelectronic ions in the series PaO_2^+, UO_2^{2+}, NpO_2^{3+}, PuO_2^{4+} can be considered.[98] In the maximum overlap model, linear spatial coordination of the nuclei corresponds to either *fd* or *fs* hybridisation, and angular coordination corresponds to *ds* hybridisation. This means that if in the actinide ion An^{z+} in the electron configuration of the ground state there is a closely-lying *d* or *s* level, the dioxo-cation AnO_2^{z+} obtained will be stable in the linear coordination. The energies ε of the transfer of an *f*-electron from the ground state to the excited electron configuration of lowest energy can be compared for the isoelectronic ions Pa^+, U^{2+}, Np^{3+}, and Pu^{4+} (Table 10). For Pa^+, excitation into the electron configuration f^3d or f^3s requires a greater expenditure of energy than excitation into the configuration f^2ds, corresponding to an angular molecule.[20–22] The preference for angular coordination distinguishes the protactinium ion from other actinyl ions. For the U^{2+} ion, the electron configuration of the ground state is $f^3d(^5L_6)$. It coincides with the electron configuration of the U^{2+} ion in the uranyl group.[99,100] Thus the doubly-charged uranium ion is able to adopt linear coordination without the expenditure of energy on *fd* hybridisation and without the participation of inner 6*p* orbitals (Table 10).

Table 10. Excitation energies (10^{-3} E, cm^{-1}) for An^{z+} in AnO_2^{z+}.[98,107]

Electron configuration	PaO_2^+	UO_2^{2+}	NpO_2^{3+}	PuO_2^{4+}
f^3d	18.04	0.00	31.60	47.00
f^2ds	1.20	—	—	—
		UO_2^+	NpO_2^{2+}	PuO_2^{3+}
f^1d		12.50	4.10	44.00
f^2ds		0.289	41.00	—
			NpO_2^+	PuO_2^{2+}
f^2d			12.80	9.80
f^1ds			0.49	57.00

It is of interest to compare the geometry of the UO_2^{2+} ion with that of the MoO_2^{2+} or WO_2^{2+} ions. Thus for the doubly-charged molybdenum ion [ground state $d^4(^5D)$], the first excited state $d^3s(^5F)$ corresponds to angular coordination and $\varepsilon \cong 30000$ cm^{-1}, whereas the excited d^3p state corresponding to linear coordination, is higher, $\varepsilon \cong 75000$ cm^{-1}.[101] Thus the dioxo-cations of the transition elements and the corresponding actinides evidently have different geometries.

The electron configuration of the ground state of the triply-charged neptunium ion and the quadruply-charged plutonium ion is $f^4(^5I)$. The energy of excitation of an *f*-electron into the *d*-level is $(38 \pm 7) \times 10^3$ cm^{-1} for Np^{3+} and 47×10^3 cm^{-1} for Pu^{4+}.[20–22] This leads to the qualitative conclusion that for the isoelectronic linear actinyl ions UO_2^{2+}, NpO_2^{3+}, and PuO_2^{4+}, the stability decreases on going from uranium to plutonium. The high excitation energy and the high electron affinity, greater than for the PuO_6^{4-} oxyanion and the PuO_4 molecule, make the cationic form of plutonium PuO_2^{4+} unstable. The published range of values for the energy of excitation of Np^{3+} into the f^3d-state is fairly wide, however: 31×10^3 $cm^{-1} \leqslant \varepsilon \leqslant 45 \times 10^3$ cm^{-1}.[20,21] Attempts to measure this quantity have a long history. In 1960, Carnall and Cohen[102] found from the absorption spectra of Np^{3+} in 1 M $HClO_4$ that the value of ε ($f^4 \rightarrow f^3d$) lies in the range 31×10^3–43×10^3 cm^{-1}. In 1965, Marcus and Shiloh[103] detected in the absorption spectra of neptunium(III) in concentrated solutions two intense bands at 26040 cm^{-1} and 32050 cm^{-1}, which they assigned to the $f^4 \rightarrow f^3d$ electron transition. The absorption and emission spectra of single crystals of $LaCl_3$ containing $NpCl_3$ were obtained in 1967.[104] A large group of bands, assigned to *ff* transitions, was detected in the range 5000–25000 cm^{-1}, and it was concluded that the energy of the $f^4 \rightarrow f^3d$ transitions lies above 25000 cm^{-1}. Recently, Carnall and co-workers[105] recorded the low-temperature absorption spectrum of $NpCl_3$ and $NpBr_3$ in the range 3300–43000 cm^{-1}. The spectra of both compounds showed broad intense bands in the range 26000–32 000 cm^{-1}, assigned to *fd* transitions. Nugent and co-workers,[22] on the basis of a systematic treatment of low-lying electron configurations, calculated the energy of excitation into different electronic states of the actinides and their ions. According to their calculations,

the excitation energy of the $f^4 \rightarrow f^3d$ transition for Np^{3+} is 31600 cm^{-1}. Finally, Carnall, Fried, and Wagner,[106] on the basis of the recorded spectra of the triply-charged ions of the elements from U to Cf in matrices, concluded that the lowest energy of excitation into the f^3d state for Np^{3+} is 26000 cm^{-1}. For comparison, it may be noted that the excitation energy of the transition $f^7 \rightarrow f^6d$ for Am is 23.9×10^3 cm^{-1} [22] or $(24 \pm 3) \times 10^3$ cm^{-1}.[20,21] Since AmO_2^+ exists, although it is less stable than other doubly-charged actinyl ions, it might be thought that NpO_2^{3+} might exist. There are two factors, however, determining stability: the ratio of the energies of the AO of the central atom and the ligands and their degree of overlap. The present authors[107] calculated the radial wavefunctions and energies of the valence AO for An^{z+} ($z = 0-5$) using a relativistic version of the Hartree–Fock method, and obtained the following results.

1. For the doubly-charged ions of the elements of the first half of the actinide series, the energy of a 5*f* orbital lies in the range 15–20 eV, that is it is close to the energy of the 2*s* and 2*p* orbitals of the oxygen atom.
2. The energy of a 5*f* orbital of the triply-charged actinide ions is much lower than that of the 2*s* and 2*p* orbitals of the oxygen atom.
3. The overlap integrals of the valence AO of the triply-charged actinide ions with the AO of oxygen are small, since the 5*f* orbitals are greated contracted, and the 5*f* electrons tend to remain localised.

All this prevents the formation of a stable NpO_2^{3+} cation, not to mention PuO_2^{4+}, since with further increase in the charge, the 5*f* electrons are localised to an even greater extent.

The isoelectronic series UO_2^+, NpO_2^{2+}, and PuO_2^{3+} can be considered. It has been established experimentally[21] that for the singly-charged uranium ion the ground state is $f^3s^2(^4I_{9/2})$; its first excited state $f^3ds(^6L_{11/2})$ lies only 289 cm^{-1} above the ground state, that is it almost coincides with the ground state, but the next excited state $f^4s(^6I_{7/2})$ lies 4664 cm^{-1} above the ground state.[20-22]. The linear coordination of the nuclei in UO_2^+ can apparently be non-rigid under certain conditions; the main condition is a low effective charge on the uranium atom, not exceeding +1.5. It may be assumed that in compounds with a uranyl group containing uranium(VI) and donor ligands, which decrease the effective charge on the uranium atom, possible deviation from the linear structure is not excluded. The energies of the transition for the doubly-charged neptunium ion into excited states correspond to a stable state and linear coordination of the nuclei in NpO_2^{2+}. The plutonyl ion PuO_2^{3+} is unstable for the same reason as NpO_2^{3+}.

A noteworthy feature is that the cationic forms examined here are three-atom systems which do not have ligands (or solvent molecules) in the equatorial plane. Donor ligands, which increase the electron density on the central atom and decrease the effective charge, would lead to stabilisation of the triply-charged cationic forms.

In a number of experimental papers[108] it has been suggested that in acidic media, septavalent Np exists as the singly-charged cation NpO_3^+. It was of interest to use quantum-chemical ideas to examine different geometric forms of this cation and to estimate the possibility of its existence as an independent oxo-group.[109] The method used was the X_α scattered wave method in the model of touching spheres. The criterion for the central metal atom being chemically combined with the oxyger atoms surrounding it is the existence of a minimum on the potential energy curve. This is equivalent to the statement that in a certain range of interatomic distances there is a strictly determined set of filled molecular levels, determined by the symmetry point group of the molecule. Since the dependence of the total energy of a molecule on the interatomic distance cannot be determined reliably in the X_α method, the possibility of existence and the stability of the NpO_3^+ cation being considered was estimated from the viewpoint of the existence of the correct standard electronic structure.[109] Three geometric configurations of NpO_3^+ were examined:[109] a *T*-shaped structure with symmetry C_{2v}, a pyramidal structure with symmetry C_{3v}, and a planar triangular structure with symmetry D_{3h}. The calculation showed that NpO_3^+ cannot exist as an independent stable oxo-group of septavalent Np, in contrast to the analogous oxo-cations of the septavalent *d* transition metals, for which both the planar triangular configuration and the pyramidal configuration exist.

5. The Use of the Principle of Orbital Symmetry to Explain the Mechanism of Cation–Cation Interactions

After Woodward and Hoffmann had demonstrated the effectiveness of the application of the principle of orbital symmetry to explain reaction mechanisms in organic chemistry, this principle became a fundamental theoretical concept.[110] The present authors attempted to apply the principle of preservation of orbital symmetry to cation–cation reactions in the chemistry of the actinides.

It has been established that actinides(V) AnO_2^+, where An = U, Np, Pu, and Am, tend to react with various "active" cations, in particular UO_2^{2+}, Fe^{3+}, In^{3+}, and Th^{4+}.[110-115] A number of regular features have been established experimentally, and can be explained on the basis of quantum-chemical considerations: only actinyl ions containing actinides(V) tend to undergo cation–cation interaction (CCI); the PuO_2^{2+} ion, isoelectronic with NpO_2^+, does not react with UO_2^{2+} ions even in 3 M uranyl perchlorate solution; the degree of CCI of UO_2^{2+} with AnO_2^+ decreases with increase in the atomic number in the series: $UO_2^+ > NpO_2^+ > PuO_2^+ > AmO_2^+$; CCI between AnO_2^+ and active cations is accompanied by a change in the electronic absorption spectrum of AnO_2^+ and by the appearance of new bands; the interaction of NpO_2^{2+} with AnO_2^+ is weaker than for UO_2^{2+}; and the degree of CCI increases with decrease in the energy corresponding to the maximum of the charge-transfer band in the absorption spectrum of the aquo-complex of the active cation.[116] In the present review, a mechanism of CCI is proposed, and a quantum-chemical explanation is given for the experimental regular features.

In the symmetry point group $D_{\infty h}$, the 5*f* atomic orbitals of an actinide atom are split into σ_u, π_u, δ_u, and Φ_u orbitals, and the 6*d* orbitals are split into σ_g and π_g orbitals. Thus for UO_2^{2+}, which has 12 valence electrons, the electron configuration of the energy levels has the form $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\Phi_u\delta_u\pi_u^*\sigma_u^*$. This configuration is preserved in all other actinyl ions AnO_2^{z+}, but with different filling numbers for the non-bonding Φ_u and δ_u levels. In solution, actinyl ions have tetragonally distorted octahedral geometry $AnO_2L_4^{z+}$ (where L represents a ligand) with symmetry point group D_{4h}. Fig. 7 shows the form of the molecular orbitals and the correlation of the symmetry of the orbitals for both point groups. On going from the free ion AnO_2^{z+} to $AnO_2L_4^{z+}$, splitting of the Φ_u level takes place, and new orbitals are added, corresponding to the interaction of the actinide with the ligands L in the equatorial plane.

The reaction between UO_2^+ and UO_2^{2+} can be considered. This interaction takes place by the overlap of the occupied molecular orbitals of UO_2^+ with unoccupied orbitals of UO_2^{2+},

and conversely. To interact, these orbitals must have the same symmetry.[110] Molecular orbital calculations for octahedral complexes containing actinides(V) and actinides(VI), AnO_6^{7-} and AnO_6^{6-}, where An = U, Np, Pu, and Am, showed showed[117] that the last occupied molecular orbital has t_{1u} symmetry. For the point group D_{4h} this corresponds to the interaction of e_{2u} and a_{2u} orbitals, and for the symmetry group $D_{\infty h}$ it corresponds to the interaction of occupied σ_u orbitals and unoccupied or partly occupied δ_u orbitals. According to calculation,[100] the energy of the occupied σ_u orbital in UO_2^{2+} is −17.75 eV, whereas the energies of the unoccupied Φ_u and δ_u orbitals in UO_2^{2+} are lower and amount to −22.88 eV and −22.72 eV respectively. This important feature determines all the specific characteristics of the interaction of the ion-containing actinides(V) and actinides-(VI), since the occupied σ_u orbital in UO_2^+ will donate electron density to the unoccupied δ_u orbital in UO_2^{2+}. The analogous interaction between the UO_2^{2+} (σ_u^2) and UO_2^+ (δ_u) orbitals is energetically unfavourable, since the donor orbital in UO_2^{2+} is much lower than the acceptor orbital in UO_2^+.

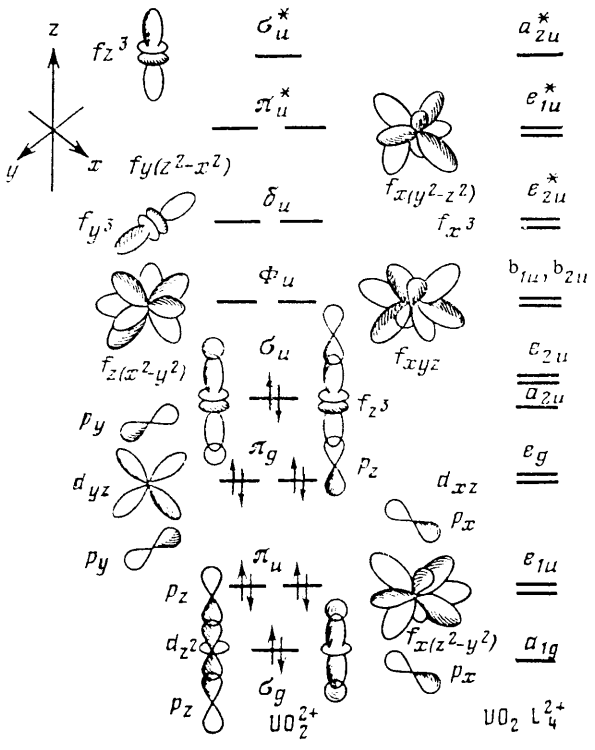


Figure 7. Qualitative energy level diagram for the uranyl ion. The change in the levels on formation of bonds with ligands L in the equatorial plane is shown on the right.[107]

This interaction scheme assumes that the ligand L in the equatorial plane is replaced, and that a U(VI)–O–U(V)–O bond is formed. The mechanism of the removal of L from $UO_2L_4^{2+}$ can be represented in terms of orbital symmetry theory.[110] Fig. 8*a* shows the symmetry of the intermediate state, which is obtained by the interaction of the antibonding orbital e_{2u}^* in $UO_2L_4^{2+}$ and the bonding orbital a_{2u} in $UO_2L_4^+$. The intermediate state symmetry requirements make necessary the rupture of the U(VI)–L bond and the formation of the U(VI)–O–U(V) bond, in which the oxygen atom of the actinyl ion containing the actinide(V) is the bridging atom. After the removal of the ligand L, the bridging oxygen atom will undergo a bonding interaction with both uranium atoms through both $f\sigma$ and $f\pi$ bonds (Fig. 8*b*).

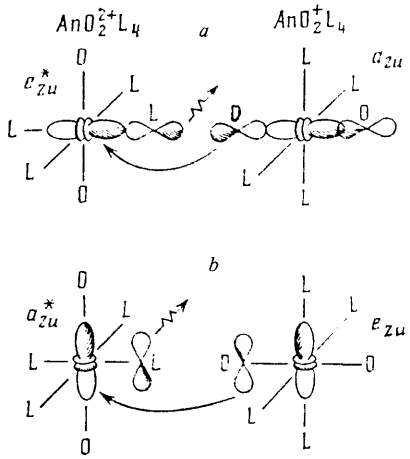


Figure 8. Interaction of the donor–acceptor type between unoccupied molecular orbitals of a uranyl complex containing uranium(VI) and the occupied orbitals of an actinyl complex containing an actinide(V):[107] *a*) σ-bond interaction, *b*) π-bond interaction.

Thus in the complexes AnO_2^+–UO_2^{2+}, the quantitative characteristic of CCI is the magnitude of the energy gap between the donor a_{2u} (or σ_u) and acceptor e_{2u}^* (or δ_u) orbitals, that is

$$E_{\sigma_u}(AnO_2^+) - E_{\delta_u}(UO_2^{2+}) = \Delta, \quad E_{a_{2u}} - E_{e_{2u}^*} = \Delta'$$

The greater Δ or Δ′, the more energetically favourable the cation–cation interaction of the donor–acceptor type. When Δ is negative, that is when the acceptor levels lie above the donor levels, CCI does not take place. On going from UO_2^+ to NpO_2^+, PuO_2^+, and AmO_2^+, the occupied σ_u^2 orbital is lowered, approaching the δ_u orbital of UO_2^{2+}, that is the magnitude of Δ decreases and the strength of the CCI decreases in the same direction.

This approach immediately explains why the PuO_2^{2+} ion, which is isoelectronic with NpO_2^+, does not react with the uranyl ion containing uranium(VI). Interaction between two UO_2^{2+} ions obviously does not take place, because $\Delta < 0$. The electron configuration of PuO^{2+} has the form $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2 \cdot \Phi_u^1\delta_u^1$. The donor level σ_u^2 in PuO_2^{2+} lies even lower than in UO_2^{2+}, and $\Delta < 0$, while $|\Delta_{PuO_2^{2+}-UO_2^{2+}}| > |\Delta_{UO_2^{2+}-UO_2^{2+}}|$, that is the UO_2^{2+}–PuO_2^{2+} interaction is even less favourable than UO_2^{2+}–UO_2^{2+}. The fact that PuO_2^{2+} and NpO_2^+ are isoelectronic does not lead to reaction, since the two *f* electrons

above the occupied "core" cloud, situated in the Φ_u and δ_u orbitals, do not interact with UO_2^{2+}, and from symmetry considerations remain non-bonding. In PuO_2^{2+}, the acceptor levels δ_u and Φ_u each contain one unpaired electron, and although these levels, as in UO_2^{2+}, are lower than the donor levels σ_u^2 in AnO_2^+, their ability to attract electron density from the O atom is lower, because of electron–electron repulsion. Thus the actinyl ions NpO_2^{2+} and PuO_2^{2+} containing actinides(VI) interact with AnO_2^+ less strongly than UO_2^{2+}. The mechanism of formation of the dimeric cation–cation complex $(NpO_2^+)^2$ ($\Delta = 0$) is fundamentally different, and involves mainly covalent interaction. Complex formation between AnO_2^{2+} and AnO_2^+ involves the modification of all the molecular orbitals in AnO_2^+. If the bond An(VI)–O with the bridging atom is sufficiently strong, the change involves both the core bonding levels and the antibonding levels of the *f* type. The change in the latter can be considered for the case of the dinuclear system UO_2^{2+}–NpO_2^+. Complex formation leads to practically no change in the positions of the b_{1u} and b_{2u} levels. Thus the ligands L take part in the formation of σ-bonds, so that the b_{2u} orbital will be non-bonding, and the b_{1u} orbital remains non-bonding from symmetry considerations. The positions of the subsequent e^*_{2u}, e^*_{1u}, and a^*_{2u} levels is influenced primarily by the non-equivalence of the Np(V)–O bonds in NpO_2^+. The internuclear distance to the bridging oxygen atom increases, the lengths of the equatorial bonds also increase, and the bond Np(V)–O with the terminal oxygen atom becomes shorter. These changes are due to the specific manifestation of the *trans*-effect in the actinides,[59,118,119] which is the opposite of the *trans*-effect in the transition elements. As a result, the energy of the e^*_{2u} level corresponding to $f\sigma$ interaction of Np(V) with the ligands of the equatorial plane, increases. The energy of the level $\sigma_u = f_z^3 + \phi_1 + \phi_2$ decreases, since one ϕ_2 orbital will correspond to interaction with a terminal oxygen atom, and the other will correspond to interaction with a bridging oxygen atom. The influence of these effects on the position of a level of the $f\pi$ type is less than that for the $f\sigma$ type, so that the splitting of the e^*_{1u} molecular orbital is slight, although its energy should decrease as a result of the decrease in the strength of the bond with the bridging oxygen atom. These changes influence the transitions of the *ff* type (Fig. 9). When the published interpretation[89] of the electronic absorption spectrum of NpO_2^+ is taken into account, it must be concluded that the main transitions take place from the non-bonding Φ_u and δ_u levels into the antibonding π^*_u and σ^*_u orbitals. The lowering of the e^*_{1u} level leads to a displacement of the most intense band with energy $\nu = 10\,200$ cm^{-1} towards the red range of the spectrum, and the splitting of the e^*_{1u} and e^*_{2u} levels leads to the appearance of a new band in the energy range 12000–13 000 cm^{-1}. This qualitative picture becomes much more complicated when allowance is made for the effect of spin–orbit coupling.

In the electronic spectrum of the combined UO_2^{2+} complex, the modification involves mainly charge-transfer bands. The absorption spectrum of the combined NpO_2^+ complex shows additional absorption bands, not related to *ff* transitions, since splitting of various levels takes place in the system of core orbitals, leading to a lowering of the symmetry of the complex from D_{4h} to C_{4v}.

According to this mechanism of CCI, the extent of this interaction should correlate with a number of parameters. It has already been noted that in the interaction UO_2^{2+}–AnO_2^+, where An = U, Np, Pu, and Am, the magnitude of the energy gap determines the degree of interaction. For the values of Δ, the position of the unoccupied $\sigma_u(UO_2^{2+})$ level can be used as the starting point for the measurement, so that the energy of the σ_u level in AnO_2^+ will be the principal determining parameter. The lower the energy of this level, the smaller the negative charge on the oxygen atoms, and the lower the degree of cation–cation interaction. At the same time, the lower the energy of this level, the smaller (for $\Delta > 0$) the magnitude of Δ, and the degree of CCI decreases. In the actinyl ions containing actinides(V), the effective negative charge on the oxygen atoms decreases on going from UO_2^+ to AmO_2^+. According to a published calculation[9] the electron density distribution in UO_2^+ is as follows: O(−0.915)–U(+2.83)–O(−0.915). According to calculations carried out by the present authors[120] for the octahedral oxyanions of the highest oxidation states AnO_6^{7-} or AnO_6^{6-}, where An = U–Am, with increase in the atomic number of An, the magnitude of the negative charge decreases by approximately 0.02–0.05 *e* on each oxygen atom.[120] It may be assumed[117] that in the americyl ion containing americium(V), the electron density distribution has the form: O(−0.8)–Am(+2.6)–O(−0.8).

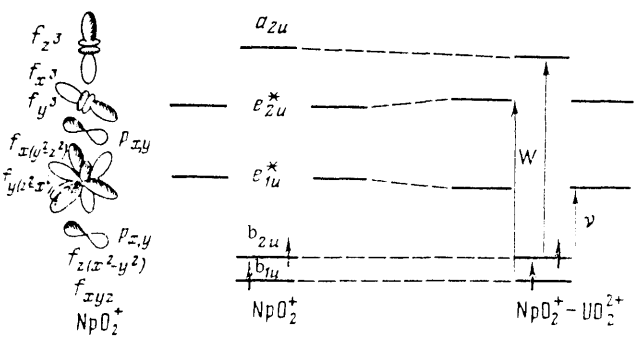


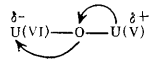
Figure 9. Splitting of the energy levels of the *f*-type in the cation–cation interaction in NpO_2^+.[107]

Thus the chemical ideas based on the electron density distribution[115] and the theoretical molecular orbital ideas about CCI coincide. The presence of an effective negative charge on the oxygen atoms in AnO_2^+ is an insufficient condition for CCI, however. In the actinyl ions AnO_2^{2+} containing actinides(VI), the oxygen atoms again have a fairly high negative charge, O(−0.27)–U(+2.54)–O(−0.27) [100] [or O(−0.3)–U(+2.6)–O(−0.3) [99]], which might have led to the transfer of electron density to the U(VI) atom and the formation of the dinuclear system ...U(VI)–O–U(VI)... The presence of an excess of negative charge on an oxygen atom of one of the actinyl ions also does not lead to interaction; thus on the basis of effective charges alone, CCI might have been expected between O(−0.3)–U(+2.6)–O(−0.3) and O(−0.1)–Am(+2.2)–O(0.1) when the uranyl ion is a ligand relative to the americyl ion. Since this interaction has not been detected experimentally, it must be assumed that the charge should be not only negative or in excess in one cation compared with the other, but that it must ensure an energetically favourable arrangement of the donor and acceptor levels σ_u and δ_u.

The degree of cation–cation interaction should correlate with other parameters in addition to the effective charges. The degree of cation–cation interaction increases with

decrease in the energy corresponding to the charge-transfer band in the aquo-complexes of the active cations.[116] Thus in the series $E_{UO_2^{2+}} < E_{Fe^{3+}} < E_{In^{3+}} < E_{Th^{4+}}$, where E is the energy of the charge-transfer band, the degree of CCI increases in the opposite direction. Thus the quantity E in the aquo-complexes is defined as $E = E_L - E^*$, where E_L is the energy of the ligand level L in ML_6^{2-} or $AnO_2L_4^{2+}$, and E^* is the energy of the orbitals of the central atom. In UO_2^{2+}, the energy E^* corresponds to the position of the acceptor level. If E_L is assumed to be approximately constant in all the complexes, the energy of the charge-transfer band will depend on the position of the level E^*, which also determines the degree of CCI: the lower this level, the lower the energy of the charge-transfer band and the greater the degree of CCI. The nature of the solvent should have a definite influence on the CCI, since the position of the levels of the central atom in the active cations depends on the interaction with solvent molecules.

Since the position of the donor level σ_u in AnO_2^+ determines to some extent the energy of the charge-transfer band in AnO_2^+ and the potential E^0(V–VI), a qualitative correlation should be observed between the degree of CCI and these quantities. The correlation can be only qualitative, since these quantities also depend on the position of the f-levels, which in AnO_2^+ have no significant influence on the CCI. A correlation between the degree of CCI and the oxidation potentials E^0(V–VI) [116] in the AnO_2^+–AnO_2^{2+} system is apparently justified, since the transfer of electron density δ in the complex (A)



corresponds to the partial reduction of the actinide(VI) atom.

In conclusion it may be noted that the position of the ions containing actinides(V) does not appear exceptional from the viewpoint of CCI. Cation–cation interaction takes place if the energy of an unoccupied acceptor orbital in one system is lower than the energy of a donor orbital in the other system, and the acceptor orbital is predominantly an orbital of the central atom. This situation may arise not only between cations, although if the acceptor system is a cation, it is known that the first unoccupied level is fairly low.

One of the criteria for the existence of CCI in complexes with identical central atoms M is apparently the ability of M to form mixed-valence compounds. Essentially, PtF_3 or $CsAuCl_3$, which in the crystalline state are made up of M(II)–M(IV) and M(I)–M(III) ions, to some extent model CCI in a crystal. About 40 elements in Mendeleev's periodic system form mixed-valence compounds,[121] in many of which an ordered arrangement of the cations with different oxidation states is produced below the critical temperature or pressure.[122] The established[123–127] criterion for the existence of a charge-ordered state $I - 2mV < 0$, where I is the energy of the one-centre electron repulsion, V the energy of the electron repulsion between centres, and m the number of nearest neighbours, also determines the stability of the cation–cation complex: in a complex of type (A), the electron–hole attraction $-2V\delta$ should be greater than the electron repulsion $I\delta$.

It can apparently be assumed that other types of cation–cation interaction will be found among the transition elements, among the actinides, and between them. If triply-charged AnO_2^{3+} cations existed, they would interact with AnO_2^{2+} according to the same regular features as AnO_2^{2+} with AnO_2^+. Three model systems with the same geometry can be considered: UO_2^{2+}, UO_2^+, and UO_2. The UO_2^{2+}–UO_2 interaction is most favourable, since for this interaction, $\Delta = 12.8$ eV;[100] the presence of two f electrons has no influence on the interaction, since in UO_2 they remain non-bonding. In the UO_2^+–UO_2 interaction, the acceptor level in UO_2^+ is partly occupied; thus the cation–cation interaction UO_2^+–UO_2 would be weaker than UO_2^{2+}–UO_2.

In the molecules of the same type UF_6, NpF_6, and PuF_6, the acceptor level in UF_6 is higher than the ligand levels in NpF_6 and PuF_6.[128] Comparison of the positions of the levels in UF_6 and UF_6^- shows, however, that the unoccupied acceptor level in UF_6 is lower than the donor level of the same symmetry in UF_6^-.[85]

6. The *trans*-Effect in the Chemistry of the Actinides

The specific features of the *trans*-effect in the chemistry of the actinides has recently attracted the attention of a number of workers.[59,118,129] Thus *trans*- and *cis*-configurations have been detected in $Cs_2UO_2Cl_4$ and $Cs_2WO_2Cl_4$ respectively. This difference was first explained[59] using the maximum overlap model. Other workers[118,129] raised the question of the fundamental difference in the *trans*-effects in $MoCl_5^-$, where M = Mo, or W, and in $UOCl_5$ (Fig. 10). The *trans*-effect observed in the uranium compounds is the direct opposite of the *trans*-effect in the analogous transition metal complexes: in the first compounds, the metal–halogen *trans*-bond is longer than the equatorial bonds, whereas in the second case the uranium–halogen *trans*-bond is shorter than the equatorial bonds.

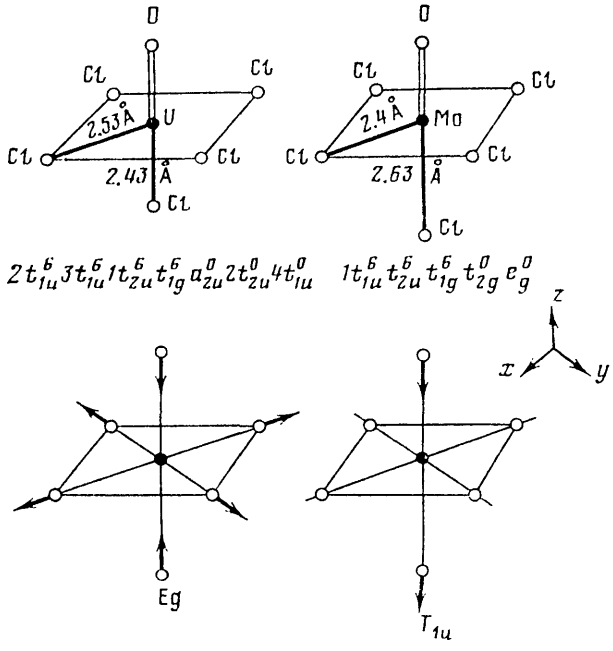


Figure 10. Comparison of the *trans*-effects in compounds of the same type formed by actinide and transition elements.[59]

Systematic MO calculations carried out by the present authors[117,119,131,132] make it possible to explain this fundamental difference using the electronic–vibrational

model of heteroligand inorganic complexes.[129] The energy of the substituted and deformed complex is represented in the form of a series with respect to powers of the normal coordinates q_ν characterising the deformation. If the energy of the non-substituted complex in the equilibrium configuration is taken as the zeroth term of the expansion, the expansion will contain a term which is linear with respect to q_ν and which leads to a change in the geometry of the non-substituted complex. In the MO method, the energy component linear with respect to q_ν has the form:[129]

$$E = 4 \sum_{\nu,o,u} \frac{\langle \psi_o H \psi_u \rangle \left\langle \psi_o \frac{\partial H}{\partial q_\nu} \psi_u \right\rangle}{\Delta_{ou}} q_\nu \quad \text{or} \quad E = kq_\nu$$

Here, ψ_o and ψ_u are the wavefunctions of the occupied and unoccupied MO respectively, Δ the magnitude of the energy gap between these MO, and H the one-electron substitution operator.

The main qualitative difference between actinide complexes and transition metal complexes of the same type is the difference in the sequence of the MO (see Fig. 10). As a result, the active mode leading to distortion will be a mode of E_g symmetry in the actinide complexes, and a mode of T_{1u} symmetry in the complexes of d transition elements. Using calculations for oxygen compounds, in particular UO_6^{6-}, it can be shown that the coefficient k in the expression for E is greater than zero in those cases where the $1t_{2u}$ and $2t_{2u}$ molecular orbitals mix as a result of the influence of the vibrational mode E_g. This means that when four substituents are introduced into UO_6^{6-} along the x and y axes, that is $UO_2L_4^{n-}$, the decrease in the total energy corresponds to $q_\nu < 0$, or in Cartesian coordinates: $q_\nu = 1/\sqrt{12}\ (2z_1 - 2z_4 - x_2 + x_5 - y_3 + y_6)$. A negative value for q_ν corresponds to an increase in the length of the equatorial bonds and a decrease in the length of the axial bonds.

This conclusion is confirmed by X-ray diffraction data for compounds containing the uranyl group. In UO_6^{6-}, the U–O distance is 2.08 Å, and in $UO_2L_4^{n-}$ this distance is 1.7–1.8 Å, whereas the U–L distances are much greater than 2.08 Å, for molecules with different ligands: NO_3^-, H_2O, $(Et_2ONCO)^-$, $MeCOO^-$, CO_3^{2-}.[133] Using the same approach in an examination of mono-substituted $UOCl_5^-$, the present authors took UCl_6 as a basis and obtained an increase in the length of the equatorial internuclear distances U–Cl compared with the U–Cl *trans*-bond.[59] In the d^0 complexes of molybdenum and tungsten, the last occupied t_{1u} and t_{2u} orbitals are mixed with the unoccupied t_{2g} orbital by a vibrational mode of symmetry T_{1u}, leading to the opposite change in the distances. In systems with the electron configuration f^n, the *trans*-effect should decrease with increase in the number of f-electrons. For those complexes for which the f-levels are occupied, the *trans*-effect should be the same as in compounds of the d-elements. In complexes with partly occupied f-levels, both vibrational modes may be active, so that the resulting effect may be extinguished.

IV. INFLUENCE OF RELATIVISTIC EFFECTS ON THE PROPERTIES OF THE COMPOUNDS OF THE HEAVY ELEMENTS

It is only in recent years that objective conditions have been created for studying the influence of the relativistic effect on the properties of the compounds of the heavy elements. A stimulus for this study was provided by the development of calculation methods and computing techniques, and also the practical interest in compounds of the heavy elements. It has been suggested[134,135] that the main anomalies in the second half of Mendeleev's table are due to the relativistic effect. These anomalies are the unique properties of gold compared with copper and silver, and of mercury compared with cadmium and zinc, the lanthanide contraction, the inert pair effect, the unique properties of the 6+ oxidation state of uranium, neptunium, and plutonium, the influence of spin–orbit coupling on magnetic properties, for example in Os(VI) compounds, the tendency towards stabilisation of the oxidation states from III to I in the indium subgroup and from IV to II in the carbon subgroup on going to the heavy elements, etc.

When it becomes necessary to take account of a given effect, attempts to explain many regular chemical features on the basis of this effect appear quite natural. This was the case, for example, with the excited nd orbitals of the atoms of phosphorus, sulphur, chlorine, and xenon. It was later found that the part played by nd orbitals for the atoms of these elements had been greatly overestimated.

Another outstanding example relates to the problem of the localisation and delocalisation of electrons. The extensive application of MO methods in calculations for molecules and the zone scheme for the solid state has practically displaced calculation schemes in which account is taken of localised states. A step back has now been taken, and the Heitler–London scheme is again beginning to be used.

The part played by relativistic effects is undoubtedly important, but it apparently should not be overestimated. In the discussion of the influence of relativistic effects on the properties of the heavy elements, it seems appropriate to distinguish three cases, where the relativistic effect: 1) completely determines the property or feature; 2) increases its strength; and 3) acts in a direction opposite to the orbital effect. In the properties of the heavy elements, the relativistic effect appears through the relativistic contraction of the $s_{1/2}$ and $p_{1/2}$ clouds, spin–orbit splitting, and destabilisation of d- and f-electrons.[134] The first effect is due to the fact that the mass of an electron depends on its velocity, the second is due to the splitting of the energy levels corresponding to the quantum numbers j, and the third is due to the high values of the angular momenta of the d- and f-electrons, the weaker attraction to the nuclei, and the more diffuse character. These effects lead to the high stability of the uranyl ion and the sexavalent forms of uranium, neptunium, and plutonium.[135]

Generally speaking, the high stability of the uranyl ion is also explained within the framework of the simple MO method, since this system contains 12 valence electrons, which occupy all the bonding MO, and the antibonding orbitals remain unoccupied. In the series of U(VI) compounds there are stable and less stable systems: on going along the series UO_4^{2-}, UO_6^{6-}, UO_2^{2+}, the stability increases, although the relativistic contraction of the 7s orbital and the opening of the 5f orbitals are everywhere the same. The properties of the compounds of U, Np, and Pu in the 6+ oxidation state can also be explained within the framework of relativistic approximations, that is they do not belong to those "specific" properties which cannot be understood even qualitatively without allowance for relativistic effects.

The influence of the relativistic spin–orbit effect on the stability of lanthanides and actinides in the 2+, 3+, and 4+ oxidation states and the tendency to form mixed-valence compounds and new oxidation states has been examined.[95,96,136,137] It was shown above that the oxidation potentials correlate with the excitation energy $E(f^n \rightarrow f^{n-1}d)$: a

high excitation energy "hinders" the oxidation, and the ion remains in the original configuration f^n, and a low excitation energy facilitates oxidation and the change to the state with the electron configuration $f^{n-1}d$. Thus a high spin–orbit splitting energy, E_{so}, in the f^n electron configuration, which brings the f^n and f^{n-1} electronic states "closer together", increases the tendency for the oxidation state to increase.

Table 11 gives the values of E_{so} and E_{fd} for the f^n electron configuration of the doubly-charged actinides. For uranium and neptunium, $E_{so} > E_{fd}$, so that the excited f^{n-1} states overlap with the terms of the f^n states. This leads to unstable bivalent forms for uranium and neptunium. For plutonium, the bivalent state is more stable, since for it, $E_{so} < E_{fd}$. For americium, $E_{so} \ll E_{fd}$, and the stability of the bivalent form reaches a maximum value in the first half of the actinide series. For curium, as for uranium and neptunium, $E_{so} > E_{fd}$, so that the bivalent state is unstable. For berkelium, $E_{so} \cong E_{fd}$, which corresponds to an increase in the stability of the bivalent form. For californium, $E_{so} < E_{fd}$, and for einsteinium, fermium, mendelevium, and nobelium, as a result of the decrease in E_{so} and the increase in E_{fd}, this inequality is preserved and increases. This leads to an increase in the stability of the bivalent state in the second half of the actinide series.

Table 11. Energies E_{so} and E_{fd} and the oxidation potentials E^0(II–III).[137]

An	n	Term	$10^{-3}E_{so}$, cm^{-1} (Ref.24)	$10^{-3}E_{fd}$, cm^{-1} (Ref.96)	E^0(II-III), V (Ref.58)
U	4	$^5I_{4-8}$	14.27	0.00	4.7
Np	5	$^6H_{5/2-15/2}$	13.74	4.10	4.7
Pu	6	$^7F_{0-6}$	9.87	13.70	3.5
Am	7	$^8S_0$	0.00	23.90	2.3
Cm	8	$^7F_{6-0}$	12.24	7.10	4.4
Bk	9	$^6H_{15/2-5/2}$	19.76	18.90	2.8
Cf	10	$^5I_{8-4}$	24.84	27.80	1.6
Es	11	$^4I_{15/2-11/2}$	21.71	30.20	1.3
Fm	12	$^3H_{6-4}$	15.25	40.10	1.1

Table 12. Energies E_{so} and E_{fd} and the oxidation potentials E^0(II–III).[137]

Ln	n	Term	$10^{-3}E_{so}$, cm^{-1}	$10^{-3}E_{fd}$, cm^{-1}	E^0(II-III), V
Nd	4	$^5I_{4-8}$	6.305	13.88	2.6
Pm	5	$^6H_{5/2-15/2}$	6.189	14.85	2.6
Sm	6	$^7F_{0-6}$	4.540	23.48	1.6
Eu	7	$^8S_0$	0.000	34.62	0.3
Gd	8	$^7F_{6-0}$	5.789	−2.19	3.9
Tb	9	$^6H_{15/2-5/2}$	10.208	8.97	3.7
Dy	10	$^5I_{8-4}$	13.497	17.52	2.6
Ho	11	$^4I_{15/2-11/2}$	15.035	16.87	2.9
Er	12	$^3H_{6-4}$	10.313	15.80	3.1

The stabilities of Ln(II) and Ln(III) can be compared analogously (Table 12). The successive decrease in E_{so} in the first half of the series and the increase in E_{fd} indicate gradual stabilisation of the bivalent state. This approach makes it possible not only to understand the regular features of the change in the oxidation potentials but also to answer the question of why they have different absolute values for corresponding lanthanides and actinides. Thus in the first halves of the series (U–Am and Nd–Eu), the relationship $E^0(\text{II–III})_{Ln} < E^0(\text{II–III})_{An}$ is preserved. For neodymium and promethium, $E_{so} < E_{fd}$, whereas for uranium and neptunium, $E_{so} > E_{fd}$. The difference $E_{fd} - E_{so}$ is much smaller for plutonium than for samarium, and E_{fd}(Am) < E_{fd}(Gd).

In the second half of the actinide series, gradual stabilisation of the bivalent states takes place, whereas in the second half of the lanthanide series this regular feature is not observed, the break in the trend taking place at holmium. Comparison of holmium and einsteinium shows a vast difference: for holmium, $E_{so} \cong E_{fd}$, whereas for einsteinium, $E_{fd} - E_{so} \cong 10000$ cm^{-1}. Similarly, for fermium, $E_{fd} - E_{so} \cong 25000$ cm^{-1}, whereas for erbium this quantity is ~5000 cm^{-1}. This difference is responsible for the difference in the oxidation potentials E^0(II–III) for the lanthanides and actinides. In addition to the difference in the oxidation potentials, this leads to the situation where states with mixed oxidation numbers are not observed in the second half of the actinide series, whereas at the end of the lanthanide series, thulium shows mixed oxidation states Tm(II)–Tm(III) in many compounds.

Table 13. Energies E_{so} and E_{fd} for the triply-charged lanthanides and the oxidation potentials E^0(III–IV).[137]

An	$10^{-3}E_{so}$, cm^{-1} (Ref.24)	E^0(III-IV), V (Ref.58)	$10^{-3}E_{fd}$, cm^{-1} (Ref.22)	Term	$10^{-3}E_{fd}$, cm^{-1} (Ref.22)	E^0(III-IV), V (Ref.58)	$10^{-3}E_{so}$, cm^{-1} (Ref.24)
Th	11.000	3.7	—	^2F	49.4	−1.8	—
Pa	11.482	2.00	26.7	$^3H_{4-6}$	61.3	−3.4	5.054
U	15.541	−0.63	27.1	$^4I_{9/2-15/2}$	70.4	−4.6	6.953
Np	17.552	−0.15	31.6	$^5I_{4-8}$	71.6	−4.9	7.982
Pu	16.625	−0.97	35.6	$^6H_{5/2-15/2}$	72.5	−5.2	7.687
Am	11.770	−2.34	45.0	$^7F_{0-6}$	81.0	−6.4	5.542
Cm	0	−3.1	55.1	$^8S_0$	92.0	−7.9	0
Bk	14.305	−1.64	38.3	$^7F_{6-0}$	55.1	−3.3	6.966
Cf	22.424	−3.2	50.0	$^6H_{15/2-5/2}$	66.6	−5.0	12.181
Es	27.466	−4.5	58.8	$^5I_{8-4}$	74.6	−6.2	15.979
Fm	24.850	−4.9	61.1	$^4I_{15/2-11/2}$	73.9	−6.1	17.678
Md	17.358	−5.4	63.0	$^3H_{6-4}$	72.7	−6.7	11.359

For the triply-charged ions of the lanthanide series, E_{fd} is much greater than E_{so}, so that the energy of spin–orbit splitting should not have a significant influence on the oxidation potentials (Table 13). The situation is completely different in the actinides: for protactinium, E_{so} is close to E_{fd}; for uranium, $E_{fd} > E_{so}$, but they are similar; for Np and Pu, E_{fd} increases slowly, and at the same time E_{so} also changes little. This corresponds to gradual destabilisation of the 4+ oxidation state. On going to curium, E_{so} decreases, and E_{fd} increases sharply, leading to a further decrease in the potential E^0(III–IV). As a result of the decrease in E_{fd} and the increase in E_{so}, the 4+ oxidation state is more stable for berkelium than for curium and americium. E_{fd} for californium is intermediate between the values for Am and Cm, but E_{so} is much larger than for

these elements. The absolute magnitude of the potential E^0(III–IV) for californium should apparently be less than 3.2 V.

The magnitude of the spin–orbit splitting of the ground state term of the f^n electron configuration can be related to the stability and geometry of the actinyl groups. It was shown above that if an actinide ion An^{z+} has closely-situated d- or s-levels, the resulting dioxo-cation will be stable for linear coordination of the nuclei. A high value of E_{so} for An^{2+} corresponds to stability of the linear AnO_2^{2+} system. On going from U^{2+} to Am^{2+}, both effects, orbital and relativistic, act in the same direction: E_{so} decreases, and E_{fd} increases, that is the stability of the actinyl groups decreases. For doubly-charged uranium, the most favourable situation is created for the formation of the dioxo-cation: $E_{fd} = 0$, and E_{so} is greater than for Np, Pu, Am, and Cm. UO_2^{2+} does not contain antibonding electrons. All this together determines the stability of the uranyl group. Beginning from NpO_2^{2+}, the number of antibonding electrons increases, so that CmO_2^{2+} should have the electron configuration $\sigma_g^2\pi_u^4\pi_g^4\sigma_u^2\Phi_u^4\delta_u\pi_u\sigma_u$, when the antibonding Φ_u level is completely occupied. In CmO_2^{2+}, however, the antibonding effect due to the four electrons in the Φ_u level is to some extent quenched by the marked spin–orbit effect and the small expenditure of energy in fd hybridisation, so that the CmO_2^{2+} cation is stable.

A comparative analysis of E_{so} and E_{fd} helps to explain why lanthanyl groups are not obtained. For doubly-charged neodymium, promethium, and samarium, the values of E_{so} are small, and $E_{fd} > E_{so}$, whereas for their analogues uranium, neptunium, and plutonium, on the contrary, $E_{fd} < E_{so}$. The values of E_{so} and E_{fd} are similar only at the end of the lanthanide series (Gd, Tb, Ho, Er). Although in the lanthanyl groups of these elements after gadolinium the next antibonding level δ_u is occupied, decreasing the strength of the bond, the decrease in strength should be less than that for their actinide analogues, since the crystal field splitting for the 4f levels is less than that for the 5f levels. In any case, the formation of lanthanyl groups in the second half of the lanthanide series cannot be regarded as impossible.

Thus on the basis of a scheme taking account of the relativistic splitting of the f^n electron configuration and the excitation energy E_{fd}, it is possible to explain a number of important regular features of the electronic structure of the lanthanides and actinides: the gradual stabilisation of the bivalent state in the first half of the lanthanide series and in the second half of the actinide series; the absence of gradual stabilisation of the bivalent state in the second half of the lanthanide series; the marked difference in the oxidation potentials E^0(II–III) in the first halves of the lanthanide and actinide series; the formation of states with mixed valence at the end of the lanthanide series, and the absence of these states at the end of the actinide series; the fundamental difference in the stability of the 4+ oxidation state for the actinides and lanthanides; and possible stabilisation of lanthanyl groups at the end of the series.

In all cases examined, the two effects act in the same direction. The relativistic effect is greater for the lower oxidation states E^0(II–III), since the values of E_{so} and E_{fd} are comparable. The two effects separately give qualitatively the change in the oxidation potentials, but the orbital effect also gives the quantitative relationship. It can apparently be stated that the relativistic effect does not determine the regular features, although it makes a significant contribution to the quantitative characteristics. The influence of the relativistic effect on the states of atoms in higher oxidation states is weakened, since the orbital effect suppresses the relativistic effect, particularly for the tervalent lanthanides. For the actinides, however, the relativistic effect may be significant in the estimation of the oxidation potentials E^0(III–IV), as clearly confirmed for californium.

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Thus quantum chemistry is finding the most varied applications in the study of the electronic structure and properties of the actinides, from the prediction of the possibility of existence of unusual oxidation states to the explanation of reaction mechanisms. In spite of considerable progress, however, many unsolved problems remain, particularly in the study of unique oxidation states in the second half of the actinide series, where experimental studies are made difficult by the high radioactivity and the difficulty of obtaining the elements.

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Institute of Physical Chemistry,
Academy of Sciences of the USSR,
Moscow

Translated from *Uspekhi Khimii*, 53, 1280-1303 (1984) U.D.C. 541.128:572.91:547.381

Nucleophilic Addition of CH Acids to αβ-unsaturated Aldehydes and Ketones

L.A.Yanovskaya, G.V.Kryshtal', and V.V.Kul'ganek

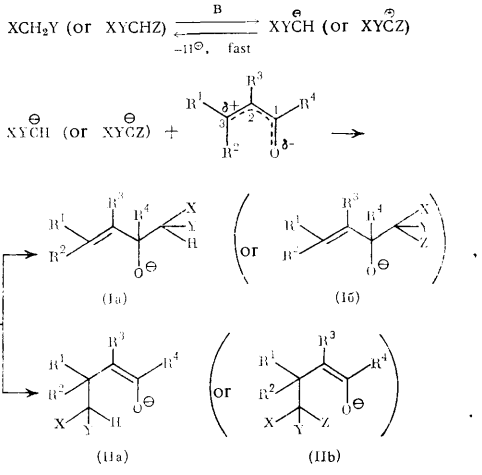
Data on the nucleophilic addition of CH acids of the type XCH_2Y and XYCHZ to αβ-unsaturated aldehydes and ketones are surveyed primarily from the standpoint of the influence of various factors on the mode of reaction (addition to the C=O or C=C bond).
The bibliography includes 116 references.

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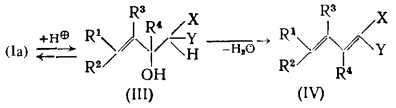
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I. INTRODUCTION

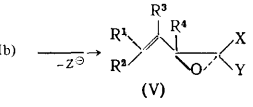
The addition of CH acids of the type XCH_2Y and XYCHZ (X, Y, and Z are atoms or groups stabilising carbanions) to αβ-unsaturated aldehydes (enals) and ketones (enones) in the presence of bases is of great synthetic importance, since it makes it possible to lengthen the carbon chain in a single stage and to introduce various substituents into the molecule. This reaction is also of interest from the theoretical point of view because, as a consequence of the delocalisation of the electron density in the C=C–C=O system, enals and enones behave as ambident electrophiles and the addition of carbanions of the type $\overset{\ominus}{C}HXY$ and $\overset{\ominus}{C}XYZ$ to these compounds can proceed via two pathways: addition to the carbon atom of the carbonyl group C(1) or to the carbon atom involved in the double bond C(3). This results in the formation of oxy-anions of types (Ia) and (Ib) or (IIa) and (IIb):



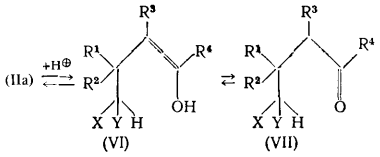
Protonation of the oxy-anions (Ia) leads to the formation of allyl alcohols (III), which are converted into conjugated dienes of type (IV) (products of the Knoevenagel reaction) on elimination of water from the 1,2-position:



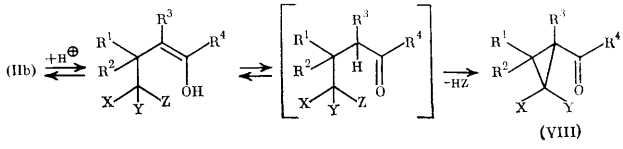
The oxy-anions (Ib) (Z = Hal) are stabilised as a result of the elimination of $Z^{\ominus}$ and cyclisation to the epoxides (V) (the Darzens reaction):



The protonation of the oxy-anion (IIa) leads to the saturated aldehyde or ketone (VII) via the enol (VI) (the Michael reaction):



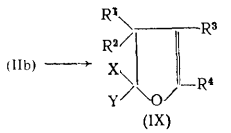
On the other hand, the protonation of the oxy-anion (IIb) and subsequent elimination of HZ from the 1,3-positions yield the cycloproane (VIII):



Thus the stabilisation of oxy-anions of type (I) results in the formation of the products of the 1,2-addition of CH acids to enals or enones (to the C=O group), while stabilisation of oxy-anions of type (II) results in the formation of products of 1,4-addition (to the C=C bond). The nature of the final reaction product depends on the nature of the CH acids, the substrate, the base used to generate the carbanions, and on the reaction conditions. All the reactions described above have been achieved and widely used to synthesise a wide variety of allyl alcohols,[1-3] conjugated dienes,[4,5] epoxides,[6] aldehydes and ketones,[7-11] and cyclopropanes,[12-17] all with functional group substituents.

The possible mechanisms of the stabilisation of the oxy-anions (IIb) examined permit the conclusion that there is yet another type of stabilisation of this oxy-anion, namely its conversion into 2,3-dihydrofuran (IX) via the elimination

of the anion $Z^{\ominus}$ with 1,5-cyclisation [compound (IX) can be formed also from the intermediate enol via the elimination of HZ]:



(IIb) (IX)

Indeed the first example of such a reaction, involving the formation of 3-formyl-2,3-dihydrofurans by the interaction of bromomalonic ester with arylidenemalonaldehydes, has been observed recently.[18]

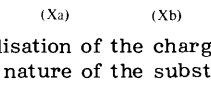
However, it is noteworthy that the addition of CH acids to enals and enones is by no means regioselective in all cases and a mixture of 1,2- and 1,4-addition products is frequently formed in various proportions. In order to ensure the regio-selectivity of the reaction and hence the possibility of the synthesis of the required products (III)–(V) and (VII)–(IX), it is necessary to investigate the influence of various factors and in the first place the structure of the CH acids, the enone, or the enal, the nature of the base used to generate the carbanions, and the conditions (temperature, solvent, and additives) on the mode of reaction and the possible further transformations of the compounds obtained.

In the present review we have considered and attempted to survey the data obtained in the last 10–15 years on the addition of CH acids of the type XCH_2Y and XYCHZ to enals and enones from the standpoint of the influence of the above factors on the mode of addition.

II. THE INFLUENCE OF THE STRUCTURE OF CH ACIDS ON THE MODE OF THE REACTION

The reactivity of CH acids is determined by the ease of deprotonation and the rate of reaction of the carbanions formed. The overall rate of addition of CH acids to enals and enones is limited by the stage involving the formation of oxy-anions. The overall rate increases with the increase in the number of electron-accepting or electronegative groups in the CH acid molecule. For CH acids of the type XCH_2Y, the activating effect of electron-accepting groups increases in the sequence RCO < HCO < ROCO < CN < RSO_3 < RSO_2 < NO_2.[7]

For carbanions generated from XCH_2Y, it is possible to adopt two extreme structures—(Xa) where the charge is localised at the carbon atom and (Xb) where the charge is fully delocalised.[19]



(Xa) (Xb)

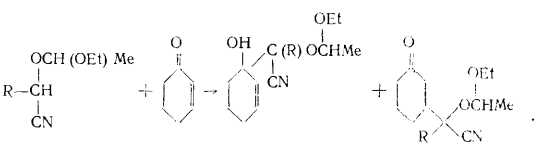
The degree of delocalisation of the charge in the carbanion is determined by the nature of the substituents in the molecule of the initial CH acid and its geometry. Within the framework of the theory of perturbations of molecular orbitals (PMO), an increase of the degree of charge delocalisation leads to an increase of the energy of the highest occupied molecular orbital (HOMO) and to an increase of the stability of the carbanion; the nucleophilicity of the carbanion and the rate of addition to the carbonyl group decrease simultaneously. Other conditions being equal, the addition of CH acids to the C=O group should be favoured by an increase of the localisation of the charge at the nucleophilic centre, by the decrease of the level of the HOMO, and by the increase of the acidity of the CH acid, i.e. the addition to the C=O bond is controlled by the charge. On the other hand, an increase of the degree of delocalisation of the charge at the nucleophilic centre, the raising of the level of the HOMO, and a decrease of the acidity of the CH acid should favour the addition to the C=C bond, i.e. it should take place under orbital control.

By the term "charge control", we understand the electrostatic interaction between the reactants. Its extent can be estimated as the product of the charges on the carbon atoms participating directly in the formation of the new bond. By the term "orbital control", we understand the energy of the interaction between the molecular orbitals of the reactants. This energy has a quantum-mechanical origin, which can be estimated from the equation

$$E_{orb} = \beta^2 C_N^2 C_E^{*2} S_{NE}^2 / (E_E^* - E_N) ,$$

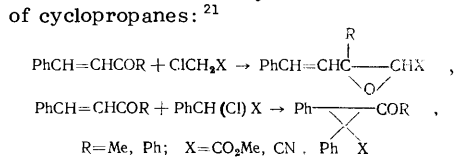
where C_N and C_E are the coefficients of the π orbitals of the carbon atoms which are directly involved in the formation of the new bond, i.e. of the π orbitals of the highest occupied molecular orbital (HOMO) of the nucleophile and the lowest unoccupied molecular orbital (LUMO) of the electrophile respectively, S_{NE} is the overlap integral between these orbitals, E_N and E_E are their energies, and β is a coefficient with the dimensions of energy.

The mode of reaction can be influenced by steric factors. Usually an increase of the bulk of the substituents R in CH acids of the type XYCHR leads to an increase of the contribution of the 1,4-addition. For example, the carbanion generated from 1-cyano-1-(1-ethoxyethoxy)ethane by treatment with lithium diethylamide in tetrahydrofuran (THF) at −78 °C forms predominantly the products of addition to the C=O bond on interaction with cyclohex-2-enone, while the carbanion generated from 1-cyano-1-(1-ethoxyethoxy)hexane gives rise to a mixture of the 1,2- and 1,4-addition products in proportions of 2.7:1.0 under the same conditions:[20]



The role of the charge or orbital control can be traced by studying the reaction of a chalcone and benzylideneacetone with the carbanion generated by treating derivatives of chloroacetic or α-chlorophenylacetic acids with a base [NaH or t-BuONa in hexamethylphosphoramide (HMP), $(Me_3Si)_2NNa$ or $(Me_3Si)_2NLi$ in THF].[21]

Regardless of the method of generation of carbanions, under kinetically controlled conditions at room temperature the reaction involves only the C=O bond in the case of $ClCH_2X$ with formation of epoxides or in the case of PhCH(Cl)X it involves exclusively the C=C bond with formation of cyclopropanes:[21]



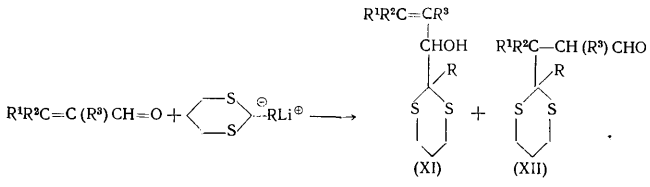
This difference between the modes of reaction is fully explicable when account is taken of the fact that the carbanions generated from $ClCH_2X$ belong to type (Xa), while those generated from PhCH(Cl)X belong to type (Xb); consequently charge control is most probable for the former reaction and orbital control for the latter reaction. In conformity with this, the rate of reaction of the carbanions

$\ominus$
$ClCHX$, where X = CO_2Me, or CN, with behzaldehyde is higher than that with benzylideneacetone,[22,23] which is associated with the higher formal positive charge on the C(1) atom in the C=O group of benzaldehyde.[24,25] Similarly the carbanions $PhC(Cl)X$, where X = CO_2Me or CN, react with the chalcone faster than with benzylideneacetone, which can be explained by the lower energy of the LUMO in the chalcone (the HOMO levels of the nucleophiles are identical in both reactions).[26,27]

In agreement with the above, the carbanions generated from 2-chloroacetates or 2-chloropropionates react with 4-t-butylcyclohex-2-enone only via the C=O group regardless of the counterion ($Na^{\oplus}$, $Li^{\oplus}$, $K^{\oplus}$, $MgX^{\oplus}$).[28] However, the carbanions generated by treating methyl 2-chloropropionate with bases add to the C=C bond in methyl vinyl ketone, although the yield of the adduct is low (~10%).[28] This can apparently be explained by the specific features of the structure of methyl vinyl ketone [the absence of steric hindrance at the C(3) atom in the vinyl group—see Section III below].

We may note that, when carbanions of the type $PhC(Cl)COOR$ or $PhC(Cl)COCH_3$ are used in the reaction with methyl vinyl ketone, the yields of the corresponding cyclopropanes increase in the former case to 58% and in the latter case to 70–75%,[29,30] which is probably associated with the increase of the orbital control with increase of the degree of delocalisation of the charge in carbanions. This can probably explain the addition of carbanions of the type $ArC(SR)Alk$, $AlkC(SeR)CN$, and other anions of the type R_3C to cyclohex-2-enone and other enones exclusively at the C=C bond under the conditions of kinetic control at −78 °C.[31,32] Carbanions with a highly delocalised charge, generated from di- or tri-nitromethane and also from dinitroethane by treatment with solid potassium carbonate, pyridine, and other bases in solution in ether, dioxan, or aqueous methanol, add to methyl styryl ketone, phenyl vinyl ketone, methyl vinyl ketone, and acrolein, also giving rise to Michael addition products in yields >90%.[33–36]

Interesting results have been obtained in the study of the reactions of enals with carbanions generated from 2-R-1,3-dithianes by treatment with lithium di-isopropylamide in a THF–HMP mixture. This resulted in a mixture of 1,2- and 1,4-adducts whose ratio depended only on the structure of the enal but not on the nature of the substituents R in the nucleophile:[37]



It follows from the data presented in Table 1 that the carbanions generated from 2-phenyl-1,3-dithiane, where there is a great possibility of charge delocalisation, react preferentially via the C=C bond, while the carbanions generated from 1,3-dithiane, where there is no such possibility, tend to add to the C=O bond. It is noteworthy that the accumulation of the substituents in the 3-position of the enal increases the content of the 1,2-adducts in the mixture (see also Section III); the reaction of 3,3-dimethylacrolein with 1,3-dithane also leads to the formation of only the 1,2-adduct, which can be explained by the steric hindrance in the attack on the 3-position by the carbanion.[37]

Interesting results have been obtained in the study of the reactions of mesityl oxide with the carbanions generated by treating the trimethylsilyl ethers of the cyanohydrins of *p*-substituted benzaldehydes with lithium di-isopropylamide in 1,2-dimethoxyethane (DME). Depending on the nature of the substituent in the *para*-position in the benzaldehyde molecule, a mixture of 1,2- and 1,4-adducts was formed in different proportions and the effect of the substituent was linearly correlated with the Hammett σ_n constants for the addition to both the C=O and C=C bonds:[38]

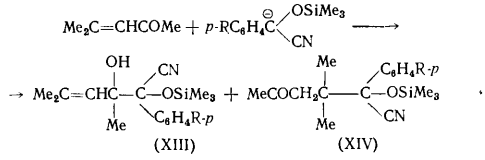


Table 1. The ratio of products (XI) and (XII) formed in the reaction of enals with 2-R-1,3-dithianes.[37]

Enal	R	*W*, %*	Content in mixture, %	
			(XI)	(XII)
MeCH=CHCHO	H	70	55	45
MeCH=CHCHO	Ph	80	5	95
CH_2=C(Me)CHO	H	70	45	55
CH_2=C(Me)CHO	Ph	80	5	95
Me_2C=CHCHO	H	55	100	0
Me_2C=CHCHO	Ph	50	65	35
PhCH=CHCHO	H	75	75	25
PhCH=CHCHO	Ph	85	35	65

*Overall yield of products (XI) and (XII).

Table 2. The influence of the nature of the *para*-substituents in p-$RC_6H_4C(OSiMe_3)CN$ on the ratio of products (XIII) and (XIV).[38]

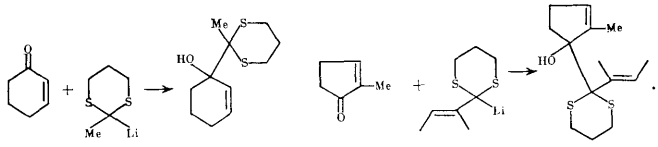
R	*W*, %*	Content in mixture, %		R	*W*, %*	Content in mixture, %	
		(XIII)	(XIV)			(XIII)	(XIV)
Me_2N	96	100	0	Cl	100	62	38
MeO	95	95	5	CF_3	100	28	72
H	92	78	22	CN	95	0	100

*Overall yield of products (XIII) and (XIV).

Table 2 presents data for the influence of the nature of the *para*-substituent in the benzaldehyde ring on the ratio of products (XIII) and (XIV) in the mixture. It is seen that the contribution of the addition to the C=O bond diminishes on passing from clearly electron-donating substituents (Me_2N, MeO) to electronegative or electron-accepting substituents (CF_3, CN). This feature can be fully accounted for by the fact that, owing to the +*M* effect, electron-donating substituents promote a greater localisation of the charge at the nucleophilic centre, while electronegative or electron-accepting substituents actually favour the delocalisation of the charge as a result of the −*I* and correspondingly −*M* effects.

However, one should note that the energy of the HOMO in p-Me_2N-$C_6H_4\overset{\ominus}{C}(OSiMe_3)CN$ is greater than the energy of the HOMO in p-$NCC_6H_4\overset{\ominus}{C}(OSiMe_3)CN$; this should promote orbital control, which is not in fact observed: in the reaction with the trimethylsilyl ether of benzaldehyde cyanohydrin, the product of addition to the C=O bond is formed exclusively. Hence one may conclude that, other conditions being equal, the mode of reaction is influenced to a greater extent by the charge delocalisation than by the height of the energy level of the HOMO (see also Section III). The ratio of compounds (XIII) and (XIV) is determined by the simultaneous influence of the charge and orbital control. The magnitude of the calculated oxidation-reduction potentials of p-$RC_6H_4CH(OSiMe_3)CN$ and enones[38] shows that the mechanism with orbital control is more probable for addition to the C=C bond rather than the mechanism with electron transfer which had been proposed on the basis of a number of data for the addition of lithium dialkyl cuprates to the double bond.[39]

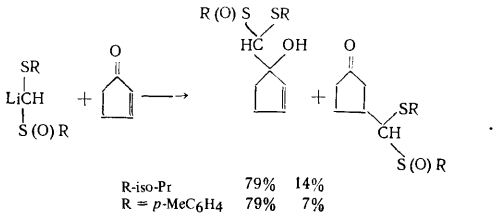
A strong influence of the structure of the nucleophile on the mode of reaction has been observed also for other examples. Thus cyclic thioacetals of the type of 1,3-dithianes, containing alkyl groups in the 2-position (for example, 2-methyl-1,3-dithiane [1]) or alkenyl groups [for example, 2-(but-2-en-2-yl)-1,3-dithiane,[40] add to cyclohex-2-enone in THF at -78 °C only at the C=O bond when the carbanions are generated by treatment with n-BuLi. The reaction with 2-methylcyclopent-2-enone proceeds in the same way:



The carbanions generated under the same conditions from aliphatic thioacetals of the type $R-CH(SR^1)[S(O)R^1]$ react via the C=C bond in enones:[41]

$$R\overset{\ominus}{C}(SR^1)(S(O)R^1) + CH_2{=}CHCOR^2 \rightarrow R^2COCH_2CH_2\underset{\displaystyle S(O)R^1}{\overset{\displaystyle SR^1}{\underset{|}{\overset{|}{C}}}}-R$$

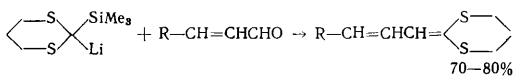
It has been shown for the addition of $CH_2(SR)[S(O)R]$ to cyclic enones using lithium di-isopropylamide in THF at -78 °C to generate the carbanion that the ratio of the 1,2- and 1,4-adducts is also influenced by the nature of the substituent R in the thioacetal component of the CH acid:[41]



R-iso-Pr	79%	14%
R = p-MeC_6H_4	79%	7%

Steric hindrance is apparently manifested in this case.

The carbanions generated from CH acids containing the trimethylsilyl group at the nucleophilic centre, for example, from Me_3SiCH_2X, where X = $P(S)Ph_2$, PPh_2, SPh, or $P(O)(OEt)_2$, or from 2-trimethylsilyl-1,3-dithiane by treatment with n-butyl-lithium always add to the C=O bond in enals and enones:[42]



The addition of CH acids to enals via a Michael reaction has been little investigated until recently. The view that nucleophiles add to enals preferentially at the C=O bond is still encountered in the literature.[4,5,8] This view is based on the fact that enals readily undergo the Knoevenagel reaction with CH acids in the presence of pyridine, piperidine, and sodium acetate.[4,5] Furthermore, enals form cyanohydrins on treatment with hydrocyanic acid.[43] The cause of the confusion is that the application of strong bases, such as alkali metal hydroxides, alkoxides, hydrides, or amides, organometallic compounds, ground alkali metals, etc. to the generation of carbanions in the Michael reaction is complicated in the case of enals by the self-condensation and polymerisation of the enals, further reactions of the addition products, the "anomalous" Michael reaction, etc.[44-46] On the other hand, the use of milder bases leads to the Knoevenagel reaction (see above).

Systematic study of the order of the addition of CH acids to enals became possible only after the introduction of the method of phase transfer catalysis into practical organic synthesis.[47-50] In this method the carbanions are generated from CH acids with a 50% solution of NaOH (or other alkalis) in a liquid–liquid system or with solid alkali (NaOH, KOH, K_2CO_3, Na_2CO_3, etc.) in a liquid–solid phase system in the presence of catalysts (onium salts, crown-ethers, etc.). The most successful variant in the reactions with enals proved to involve the application of a liquid–solid phase system [Na_2CO_3–benzene–triethylbenzylammonium chloride (TEBAC)] for the generation of carbanions from malonic, acetoacetic, and cyanoacetic esters.[51-53] Under these conditions, the mode of reaction depends greatly on the nature of the CH acid. Thus the carbanions $\overset{\ominus}{C}H(CO_2Et)X$, where X = CO_2Et or COMe, add exclusively to the C=C bond in enals without substituents in the 3-position (acrolein and methacrolein) and also to 3-monosubstituted enals (for example, crotonaldehyde, cinnamaldehyde, etc.):

$$XCH_2COOEt + R{-}CH{=}CH{-}CHO \rightarrow R{-}\underset{\displaystyle XCHCO_2Et}{\overset{\displaystyle CHCH_2CHO}{\underset{|}{\overset{|}{CH}}}}$$

X=CO_2Et, COMe; 44–75%

Table 3. Certain characteristics of malonic and cyanoacetic acids*.

Carbanion	$q_N^{\bullet\bullet}$, e	C_N	E_N, eV
$[HC(COOH)_2]^{\ominus}$	−0.435	−0.630	−4.424
$[NCCHCOOH]^{\ominus}$	−0.479	−0.660	−3.254

*Calculations performed in accordance with a CNDO/2 programme.[55]

**Here q_N is the π-electronic charge on the carbanionic centre.

The carbanions generated from cyanoacetic ester add to the C=C bond only in enals unsubstituted in the 3-position. 3-Substituted enals react with cyanoacetic ester at the C=O bond, which can be explained if account is taken of the most important characteristics[54] of malonic and cyanoacetic acids and their esters, which determine the charge and orbital control of the nucleophilic addition (Table 3).

In considering the data in Table 3, one should note that, compared with the malonic acid carbanion, the cyanoacetic acid carbanion has a significantly greater coefficient of its HOMO and a higher level of the HOMO, which should favour orbital control. However, the charge on the cyanoacetic carbanion is higher than that on the malonic acid carbanion which is responsible for the predominance of charge control, other conditions being equal. The latter probably obtains also in the reaction of 3-substituted enals with cyanoacetic esters. There is no doubt that steric hindrance due to the substituents in the 3-position in the enals also plays a major role.

It is of interest that the carbanions generated from cyanoacetic ester on treatment with potassium fluoride in acetonitrile in the presence of dibenzo-18-crown-6 ether add only to the C=C double bonds of the chalcone, forming adducts via the Michael reaction in a yield of ~90%.[56] This result is apparently associated with the fact that acetonitrile solvates the $K^{\oplus}$ ion fairly effectively and impairs its complex formation reaction with the CO group, which as a rule alters the regioselectivity of the reaction and leads to preferential attack on the 3-position of the enal.[57]

The reaction between the chalcone and ethyl 2-nitroacetate in a homogeneous medium (in toluene in the presence of 1-dimethylamino-2-hydroxy-1-methyl-2-phenylethane as the catalyst at room temperature) or in a two-phase system [in acetonitrile with KI in the presence of (2-hydroxy-1-methyl-2-phenylethyl)(dimethyl)ethylammonium bromide or (benzyl)(2-hydroxy-1-methyl-2-phenylethyl)dimethylammonium chloride as the catalyst] proceeds analogously:[58]

$$PhCH{=}CHCOPh + XCH_2CO_2Et \rightarrow \underset{\displaystyle XCHCO_2Et}{\overset{\displaystyle PhCHCH_2COPh}{|}} .$$

When X = CN, the yield is 90%, while for $X = NO_2$ the yield amounts to 10% (in a homogeneous medium) and 40% (in the two-phase system).

The presence of three stabilising substituents at the carbanionic centre frequently causes the reaction to take place only at the C=C bond of the enal or enone. Thus methyl 2,2-di(phenylthio)acetate reacts with acrolein, crotonaldehyde, etc. in DME in the presence of catalytic amounts of Triton B to form only adducts resulting from the reaction involving the C=C bond:[59]

$$R{-}CH{=}CHCHO + (PhS)_2CHCOOMe \rightarrow \underset{\displaystyle (PhS)_2CCOOMe}{\overset{\displaystyle R{-}CHCH_2CHO}{|}} .$$
24—85%

Under the standard conditions of phase transfer catalysis (CH_2Cl_2–50% NaOH solution–TEBAC with addition of NaOH solution to the mixture of components)[16,60,61] or in an alcoholic solution in the presence of sodium alkoxide,[12] enals react with bromomalonic ester to form formylcyclopropanes:

$$R{-}CH{=}CH{-}CHO + BrCH(CO_2Et)_2 \longrightarrow \underset{\displaystyle EtO_2C \quad CO_2Et}{\overset{\displaystyle R \qquad\qquad CHO}{\diagup\!\diagdown}} ;$$

R=H, Me, Ph, $(MeO)_2CH$ (yield 43–48%); R=MeCH=CH, Cl_2C=CH, PhCH=CH (yield 15–29%).

1,1,2,2-Tetra(ethoxycarbonyl)ethane is always formed in the reaction as a side product. Thus in this case the reaction involves the C=C bond. It is noteworthy that, when the alkoxide method is used, the reaction products are formed only in the case of acrolein and crotonaldehyde. The alteration of the order of mixing, i.e. the addition of the reactant mixture to a mixture of the 50% NaOH solution, the solvent, the TEBAC, results in the formation of formylcyclopropane only from acrolein, while the remaining enals polymerise under these conditions.[13] However, enones more resistant to alkalis give rise to acylcyclopropanes in high yields, for example:

$$MeCOCH{=}CH_2 + BrCH(CO_2Et)_2 \rightarrow \underset{\displaystyle EtO_2C \quad CO_2Et}{\overset{\displaystyle MeCO \qquad\qquad}{\diagup\!\diagdown}} .$$

The occurrence of the reaction at the C=C bond in the case of carbanions stabilised by three electron-accepting and electronegative substituents can undoubtedly be accounted for by the increase of the degree of delocalisation of the charge.

In a series of studies devoted to the elucidation of the order of addition of the carbanions generated by treatment of CH acids having between one and three stabilising substituents with lithium di-isopropylamide in THF or DME, the features associated with the influence of the structure of the carbanions on the mode of reaction were elucidated. It was found that highly basic ("hot") nucleophiles of the type of carbanions derived from 2-methyl-1,3-dithianes[62] or 2-(2-ethoxyethoxy)propionitrile[63] and also the salts $H_2\overset{\ominus}{C}COO^{\ominus}.2Li^{\oplus}$[64] and $N\overset{\ominus}{C}CH_2.Li^{\oplus}$[65] add irreversibly to enones even at low temperatures, giving rise to a mixture of products of reactions involving the C=O and C=C bonds. Nucleophiles such as 1,3-dithianyl-2-phenyl-lithium,[66] $NC\overset{\ominus}{C}HPh.Li^{\oplus}$,[65] or $Ph\overset{\ominus}{C}.(CO_2R)X.Li^{\oplus}$ (where R, X = H, SePh; Me, SeMe; Me, OMe; Me, Me)[69] initially add to the C=O bond; however, when the temperature is raised, the 1,2-adducts formed rearrange spontaneously to 1,4-adducts, whose thermodynamic stability is higher. Nucleophiles of the type $NC\overset{\ominus}{C}(CH{=}CHMe)OCHMeOEt,Li^{\oplus}$,[65] $Ph\overset{\ominus}{C}(R)[S(O)R^1].Li^{+}$,[68,69] and $(EtS)_2\overset{\ominus}{C}CO_2Me.Li^{\oplus}$[70] add irreversibly to the C=C bond, but, depending on the structure of the enone, there is also a possibility of the irreversible addition to the C=O bond.

In contrast to the nucleophile $Ph\overset{\ominus}{C}(CN)(OSiMe_3).Li^{\oplus}$,[38] the nucleophile $NC\overset{\ominus}{C}HP(O)(OEt)_2.Li^{\oplus}$[71,72] reacts with enones of the type $R_2C{=}CHCOMe$ at the C=O group. Nucleophiles such as 1,3-dithianyl-2-phenyl-lithium[66] or $Me_2\overset{\ominus}{C}(CO_2Me).Li^{\oplus}$[67] react analogously even in solvents of low polarity at −78 °C.

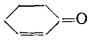
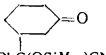
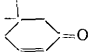
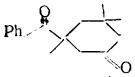
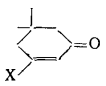
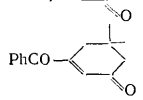
III. THE INFLUENCE OF THE STRUCTURE OF ENALS AND ENONES ON THE MODE OF THE REACTION

The direction of the nucleophilic addition of CH acids of the type XCH_2Y and XCHYZ depends on the structure of the enals. In the case of enones such a dependence is not usually observed. Table 4 presents the results of the reactions of aliphatic and cyclic enones with the carbanions generated from the trimethylsilyl ether of benzaldehyde cyanohydrin by treatment with lithium di-isopropylamide in ether. 1,4-Adducts are formed exclusively under these conditions[73] and hydrolyse smoothly and in high yields to 1,4-diketones on treatment with 2 *N* HCl, Et_3NHF, or $(PhCH_2)Me_3NF$. The method described is convenient for the synthesis of these compounds.

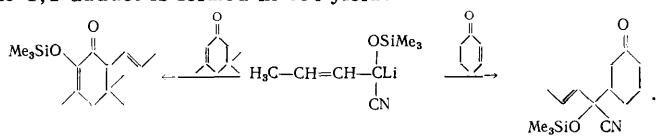
Table 4 shows that all the ketones used in the above study,[73] with the exception of 4-chloropent-3-en-2-one, form adducts in high yields. A decrease of the yield is observed when the cyclic ketones contain a substituent in the 3-position relative to the keto-group and the decrease is in

order of increase of the bulk of the substituent (Cl > EtO > Br). Apparently, the steric hindrance generated in relation to attack by the nucleophile on the 3-position plays the main role in this case. It may be that this also accounts for the absence of reaction in the case of 4-chloropent-3-en-2-one, where, apart from the methyl group, a bulky chlorine atom is present in the 3-position (in addition, account must be taken of the unfavourable influence of the +*M* effect of the chlorine atom).

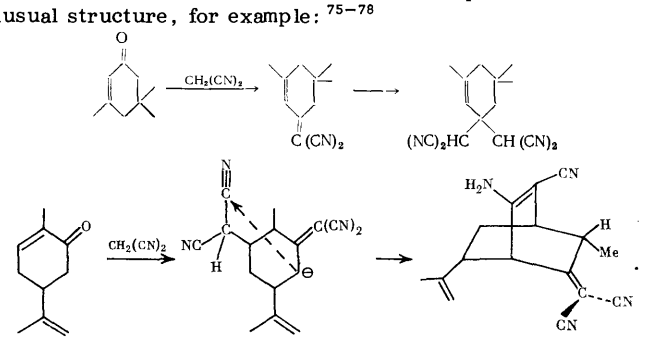
Table 4. Products of the addition of the trimethylsilyl ether of benzaldehyde cyanohydrin to various ketones.[73]

Ketone	Product of addition or subsequent hydrolysis	Yield, %
$Me_2C{=}CHCOMe$	$Me_2C(PhC(OSiMe_3)CN)-CH_2COMe$	84
$PhCH{=}CHCOMe$	$PhCH(PhC(OSiMe_3)CN)-CH_2COMe$	87
		96
$MeCCl{=}CHCOMe$	not formed	0
		45
		40 (X = Cl) 20 (X = EtO) 10 (X = Br)

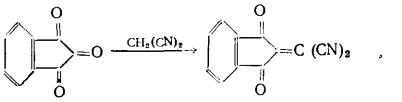
The major role of steric effects is also indicated by the interaction between the carbanion generated from the trimethylsilyl ether of crotonaldehyde cyanohydrin and cyclohex-2-enone or 3,5,5-trimethylcyclohex-2-enone in THF. In the former case the reaction proceeds via the C=C bond (the yield of the adduct is ~72%), while in the latter case the 1,2-adduct is formed in 53% yield:[74]



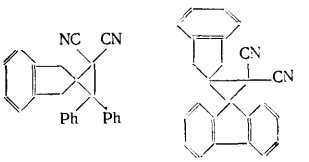
In this connection one should note that the interaction of malonodinitrile with enones in which the C=O group is sterically hindered takes place in DMF in the presence of potassium fluoride via a Michael reaction, while in the absence of steric hindrance the Knoevenagel reaction takes place initially. In a number of instances the formation of an active conjugated system under these conditions promotes the further addition of malonodinitrile to the conjugated system via the Michael reaction and the formation of products of unusual structure, for example:[75–78]



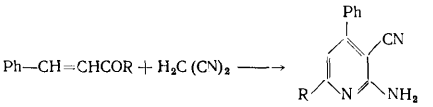
It is of interest that the uncatalysed reaction of malonodinitrile with indan-1,2,3-trione in benzene proceeds via a Knoevenagel reaction with formation of 2-dicyanomethyleneindan-1,3-dione:[79]



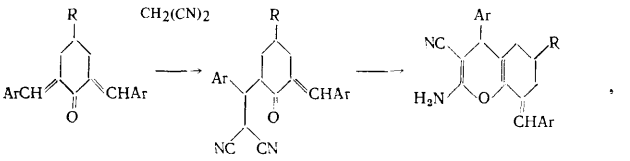
The Michael addition of malonodinitrile to enones makes it possible to introduce two cyano-groups into the molecule and to obtain new interesting compounds by further reactions. Thus 2-dicyanomethyleneindan-1,3-dione reacts with diphenyldiazomethane or 9-diazofluorene[79] to form spirocyclopropanes:



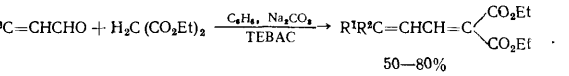
The reaction of equimolar amounts of malonodinitrile with enones in the presence of an excess of ammonium acetate leads to the formation of 4,6-disubstituted 2-amino-3-cyanopyridines in 60–70% yield:[80–81]



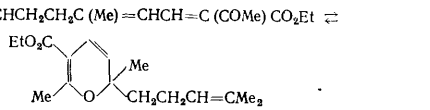
The reaction of chalcones with malonodinitrile results in the formation of 2-amino-4,6-diarylnicotinonitriles, whose hydrolysis leads to substituted nicotinamides.[82] The interaction of diarylidenecyclohexanones with malonodinitrile in the presence of sodium ethoxide or hydroxide can be used to synthesise chromones in 60–90% yield:[82]



A striking example of the influence of the structure of the substrate on the mode of the addition reaction involving enals is the interaction of malonic ester with 3,3-disubstituted enals in which the 3-position is undoubtedly sterically hindered; in this case the reaction is of the Knoevenagel type. Thus the corresponding dienes are formed from 3,3-dimethylacrolein, 3,3-dichloroacrolein, or citral:[51–53]



Citral reacts via a Knoevenagel reaction also with acetoacetic ester to give a mixture of open-chain and cyclic reaction products, which is one of the examples of valence isomerisation:[51–53,83–85]



Very interesting results have been obtained in the reaction between malonic or acetoacetic ester and ω,ω-dichloropolyenals in the C_6H_6–Na_2CO_3–TEBAC system.[53] The simultaneous formation of products of addition to both the C=C and

C=O bonds is observed in this case. Table 5 presents the ratios of the products of the reactions of ω,ω-dichloropolyenals with malonic, acetoacetic, and, for comparison, cyanoacetic esters:

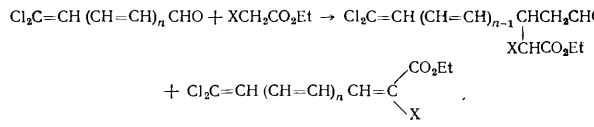


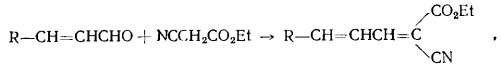
Table 5. The contents (%) of products of the addition of XCH_2CO_2Et (where X = CO_2Et, COMe, or CN) to the C=C and C=O bonds in ω,ω-dichloropolyenals. [53]

CH acid	n=0		n=1		n=2	
	C=C	C=O	C=C	C=O	C=C	C=O
$H_2C(CO_2Et)_2$	0	100	75	25	*	*
$H_2C(COMe)CO_2Et$	0	100	45	55	18	82
$H_2C(CN)CO_2Et$	0	100	0	100	0	100

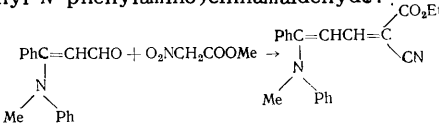
*Does not react.

Evidently, the mode of reaction is determined by the length of the chain of conjugated double bonds. The occurrence of the reaction exclusively at the C=O bond of 3,3-dichloroacrolein (n = 0) can be explained primarily by the steric hindrance in the attack by the carbanion on the 3-position. An increase in chain length naturally leads to the elimination of the steric effect of the terminal substituents and the formation of adducts via the reaction at the C=C bond becomes possible, which is in fact observed in reality in the interaction of 5,5-dichloropenta-2,4-dienal (n = 1) with malonic and acetoacetic esters, the product of the Michael reaction predominating in the former case. 7,7-Dichlorohepta-2,4,6-trienal (n = 2) does not react with malonic ester and the reaction with acetoacetic ester gives rise to a mixture in which the product of the Knoevenagel reaction predominates.

In the same system (C_6H_6–Na_2CO_3–TEBAC), sorbaldehyde, 5-phenylpenta-2,4-dienal, and 7-phenylhepta-2,4,6-trienal do not react with malonic or acetoacetic ester. Enals with markedly electron-donating substituents in the 3-position, for example, 3-dimethylaminoacrolein, also do not react with acetoacetic ester. [86] However, the interaction of enals of the type of 3-dimethylaminoacrolein, [86] 5-phenylpenta-2,4-dienal, and ω,ω-dichloropolyenals [53] with cyanoacetic ester, which most probably takes place under charge control, leads to the formation of the products of the Knoevenagel reaction:

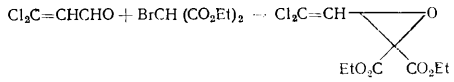


Methyl 2-nitroacetate reacts analogously at the C=O bond of 2-(*N*-methyl-*N*-phenylamino)cinnamaldehyde: [87]

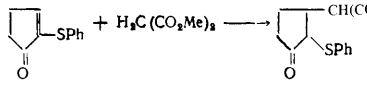


On treatment with nitromethane or cyanoacetic ester in the presence of piperidine, 2-nitro-3-phenylaminoacrolein also gives rise to 1,2-adducts. [88,89]

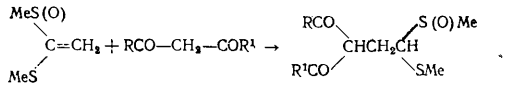
In contrast to acrolein and 3-monosubstituted enals, 3,3-disubstituted enals do not react with bromomalonic ester in the CH_2Cl_2–50% NaOH solution–TEBAC system, while in the DMF–K_2CO_3–TEBAC system the reaction is of the Darzens type. For example, 3,3-dichloroacrolein gives rise to 3-(β,β-dichlorovinyl)-2,2-di(ethoxycarbonyl)epoxyethane under these conditions: [18]



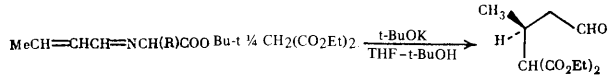
Addition to the C=C bond is apparently favoured by the presence of the thioester residue at the double bond in the α-position relative to the CO group. Thus 2-phenylthiocyclopent-2-enone very readily combines with dimethyl malonate in the presence of sodium methoxide in methanol: [90]



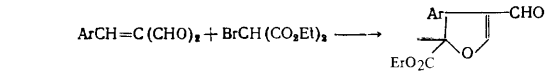
Certain keten derivatives can be introduced into the Michael reaction. Thus the interaction of keten thioacetals with the carbanions generated by treating malonic or acetoacetic ester or acetylacetone with sodium hydride in THF at −78 °C results in the formation of adducts via the reaction at the C=C bond in yields of 91–98%: [91]



In order to synthesise optically active aldehydes, the reaction involving the addition of malonic ester to aldimines, obtained from crotonaldehyde and optically active aminoacids, was employed. [92] The subsequent hydrolysis yielded (*S*)(+)-aldehydes in optical yields from 48 to 54%:



Finally we may mention yet another instance where the structure of the enal has a decisive influence on the structure of the final product. This involves the formation of formyldihydrofurans by the reaction of arylidenemalonaldehydes with bromomalonic ester in the DMF–K_2CO_3–TEBAC system: [18]



The formation of formyldihydrofurans can be explained by the possibility of the stabilisation of the anion of type (IIb) (formed in the reaction) by the elimination of $Br^{\ominus}$ with cyclisation or via the elimination of HBr from the 1,5-position of the enol formed by the protonation of (IIb) (as a consequence of the influence of the CHO group, which increases its stability, this enol can cyclise to dihydrofuran before it isomerises to a saturated aldehyde, which can be converted into a cyclopropane on subsequent elimination of HBr from the 1,3-positions).

Table 6 presents the results of the calculation of the electronic structures of the enals. Evidently, in all the enals investigated, the greatest positive charge is localised at the C(1) atom of the C=O group. Consequently, reactions whose mode is determined by the electrostatic interaction (charge control) should proceed preferentially at this atom. The highest coefficient C_E^* of the LUMO of enals is that of the π electron orbital of the C(3) atom involved in the

C=C bond. The reactions whose mode is determined by orbital control should therefore take place at the C(3) atom.[93]

Table 6. Certain characteristics of enals.[93]

Enal	$e^{\bullet}_{\sigma+\pi}$, e		$c^{\bullet}_{E}$	
	C (1)	C (3)	C (1)	C (3)
H_2C=CHCH=O	0.225	0.003	0.511	—0.576
MeCH=CHCH=O	0.225	0.060	0.461	—0.579
Me_2C=CHCH=O	0.224	0.101	0.423	—0.579
H_2C=C(Me)CH=O	0.217	—0.028	0.503	—0.567
MeCH=C(Me)CH=O	0.217	0.029	0.449	—0.572
ClCH=CHCH=O	0.232	0.124	0.485	—0.523
Cl_2C=CHCH=O	0.234	0.221	0.453	—0.613
Cl_2C=CHCH=CHCH=O	0.160	0.090	0.336	—0.475

*Here $e_{\sigma+\pi}$ are the $\sigma + \pi$ electronic charges on the atoms.

The relative contributions of the Coulombic (charge) and orbital interactions can be estimated by employing the ratio of the terms I_1/I_2, where I_1 characterises the Coulombic interaction and I_2 the orbital interaction. The data obtained for acrolein and its methyl derivatives are presented in Table 7. Evidently, in all cases the introduction of methyl groups hardly alters either ΔE or the index ratio I_1/I_2, so that the mode of reaction cannot be predicted on the basis of the relations obtained, although it does vary as a function of the nature of the reactants, which can be deduced from the experimental data discussed above.[93]

Table 7. Energy data for the reactions of certain enals with the C-anions of malonic and cyanoacetic acids.[93]

Enal	ΔE, eV		$I_1(C(1))/I_2(C(3))$
	⊖CH(COOH)$_2$	⊖CH(CN)COOH	
H_2C=CHCHO	—6.30	—5.43	3.70
MeCH=CHCHO	—6.24	—5.37	3.55
Me_2C=CHCHO	—6.16	—5.29	3.65
H_2C=C(Me)CHO	—6.26	—5.39	3.62
MeCH=C(Me)CHO	—6.13	—5.26	3.52

Notation: $\Delta E = E_N^{HOMO} - E_E^{LUMO}$, $I_1 = q_N q_E$ (π, σ) is the index of Coulombic interaction, and $I_2 = C_N^2 C_E^2/(E_E - E_N)$ is the index of orbital interaction.

The mode of the addition reaction can be significantly influenced by the steric hindrance associated with the different bulks of the H atom and the methyl group (or the chlorine atom), because the addition of carbanions to enals leads to a considerable deformation of the structure of one of the carbon atoms of the enal, which changes from planar to pyramidal as the carbanion approaches. Table 8 presents the "pyramidalisation" energies of the C(1) and C(3) centres for acrolein and its methyl and chloro-derivatives, calculated as differences between the energies of the pyramidal and planar enals. It is evident from these data that in the case of acrolein the conversion of the terminal carbon atom C(3) involved in the C=C bond into a pyramidal form is most favourable. The substitution of one of the hydrogen atoms at C(3) by a methyl group leads to a qualitative alteration of the result. The conversion of the C(1) atom of the carbonyl group into the pyramidal form is energetically more favourable; the substitution of the second hydrogen atom at C(3) by a methyl group increases the difference to 9 kcal mol^{-1}. The substitution of hydrogen atoms by chlorine atoms leads to a qualitatively similar result as the introduction of a methyl group. Thus the substitution of the hydrogen atoms at C(3) by methyl groups or chlorine favours the alteration of the mode of the addition reaction by virtue of steric factors.

Table 8. The relative* energies of the "pyramidalisation" (E) of the C(1) atom for R^1R^2C=CHCH=O (according to the data of Kryshtal' et al.[93]).

R^1	R^2	E, kcal mol^{-1}
H	H	4
H	Me	—3
Me	Me	—9
H	Cl	—1
Cl	Cl	—4

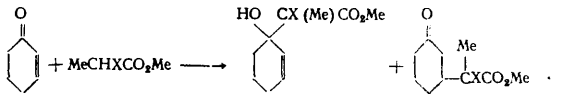
*The energy of the structure with the pyramidalised C(3) atom has been adopted as zero.

IV. CONDITIONS AND MODE OF THE REACTION

Studies in recent years have shown that the mode of addition of CH acids, including those of the XCH_2Y and XCHYZ types, to enals and enones depends very strongly on the reaction conditions—primarily on temperature, the nature of the solvent, and additives.

Temperature

The dependence of the mode of addition of CH acids to enones on temperature has been clearly demonstrated for the addition to cyclohexenones of the carbanions generated from $MeCHXCO_2Me$, where X = OPh, OMe, SPh, SMe, or Me, under the influence of lithium di-isopropylamide.[94] It was established that, under the conditions of kinetic control at −78 °C, the addition is exclusively to the C=O group (except in the case where X = SPh); on raising the temperature, it is possible to alter the mode of addition of the nucleophile (Table 9):



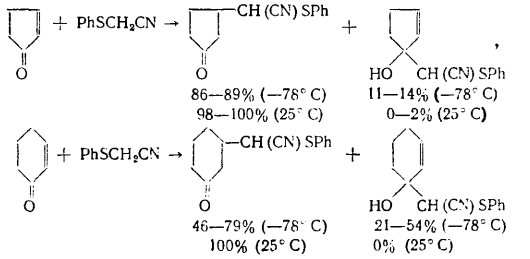
The addition of methyl 2-phenylthiopropionate takes place only in the 1,4-positions both at −78 °C and 25 °C. The introduction pf tje SMe substituent (the $-I$ and $+M$ effects)

probably increases the energy of the HOMO of the nucleophile and leads to a change from charge to orbital control. The absence of this effect when the SPh group is introduced is apparently associated with the fact that this group increases the level of the HOMO to a lesser extent, because the *n* electron pair of the S atom interacts not only with the nucleophilic centre but also with the benzene ring.

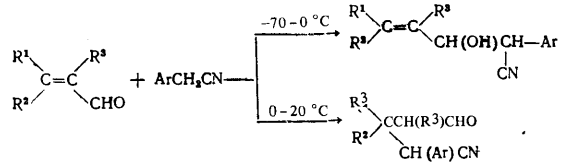
Table 9. The influence of temperature on the mode of addition of methyl 2-X-propionate to cyclohex-2-enone. [94]

X	Yield of 1,2-adduct, %		Yield of 1,4-adduct, %	
	−78° C	+25° C	−78° C	+25° C
OPh	88	—	8	84
OMe	75	5	12	62
SPh	—	—	75	86
SMe	63	—	7	85
Me	88	7	5	83

Analogous results have been obtained in the study of the addition of phenylthioacetonitrile to cyclopent-2-enone and cyclohex-2-enone in THF and in ether using lithium di-isopropylamide to generate the carbanions. [95] The 1,2-adducts are formed in appreciable amounts at −78 °C, while at room temperature the products are exclusively or mainly the 1,4-adducts:



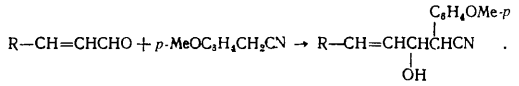
The addition of the carbanions generated from arylacetonitriles by treatment with lithium di-isopropylamide to enals in THF yields at temperatures from −70° to 0 °C the products of the reaction involving the C=O group or at temperatures from 0° to 20 °C the products of the reaction involving the C=C bond: [96]



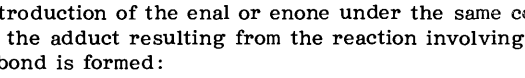
The 1,2-adducts are thus the main reaction products under the conditions of kinetic control, while the 1,4-adducts are the products under the conditions of thermodynamic control. However, the 1,4-adducts can be formed also under the conditions of kinetic control (see below).

Solvents

The very great influence of solvents on the mode of addition of nucleophiles to enones and enals has been frequently noted but has found an explanation only in recent years. [57] The most striking example is the shift of the equilibrium in the reaction of enones towards 1,4-addition in the presence of HMP. [2] Thus the interaction between *p*-methoxyphenylacetonitrile (the carbanion is generated under the influence of n-BuLi at −78 °C) and cyclohex-2-enone or enals of the type R−CH=CHCHO in THF always takes place with the dominant formation of allyl alcohols:

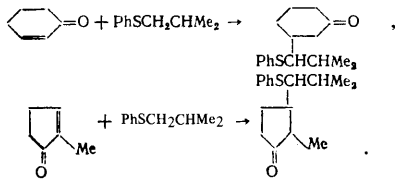


However, when HMP is added to the reaction mixture before the introduction of the enal or enone under the same conditions, the adduct resulting from the reaction involving the C=C bond is formed:

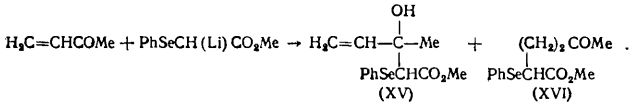


The reaction between cyclohex-2-enone or 5-isopropenyl-2-methylcyclohex-2-enone and the carbanions generated from $Me_2CHCH(SePh)(SPh)$, [2] 2-R-1,3-dithianes, 1,1-di(phenylthio)alkanes, or 1,1-di(methylselenyl)alkanes by treatment with n-BuLi takes place analogously. [97] The 1,4-adducts are formed preferentially under kinetic conditions at −78 °C (the content of the 1,2-adducts does not exceed 1–7%). This is one of the examples illustrating the possibility of the formation of the 1,4-adducts when the reaction takes place under kinetic control. The effect of HMP in this instance consists in the fact that the above solvent solvates vary effectively the lithium ions, which are known [57] to increase the regioselectivity of the process in favour of 1,2-addition under both charge and orbital control as a result of complex formation via the C=O group and the consequent decrease of the energy level of the LUMO of the enone or enal and the increase of the coefficient for the C(2) atom. Solvation interferes with complex formation to a greater extent the greater the solvating capacity of the solvent.

The addition of HMP is widely used for synthetic purposes. For example, the employment of a mixture of THF and HMP at −78 °C in the reactions of the carbanions generated by the action of n-BuLi on isobutyl phenyl sulphide with cyclohex-2-enone and 2-methylcyclopent-2-enone makes it possible to obtain satisfactory yields of the 1,4-adducts: [98]



The addition of HMP has a considerable influence also on the reaction of methyl vinyl ketone with a selenyl-substituted carbanion. [99] Thus, when the reaction is carried out at −78 °C in THF, a mixture containing 81% of compound (XV) and 19% of compound (XVI) is formed; the addition of a small amount of HMP lowers the content of compound (XV) in the mixture to 15% and increases that of compound (XVI) to 85%:



Sometimes, in order to achieve the regioselectivity of the 1,4-addition, it is necessary not only to add HMP but also to increase the reaction temperature. For example,

lithium selenoacetates add to cyclohex-2-enone in THF at −78 °C with formation of a mixture of the 1,2- and 1,4-adducts in proportions of 95:5; the addition of HMP alters the ratio to 20:80 and only an increase of temperature to −45 °C makes it possible to achieve the ratio 5:95.[99]

As a rule, highly polar protic solvents, such as water or alcohols, promote the 1,4-addition. This is also favoured by dipolar aprotic solvents (DMF, DMSO, HMP, etc.) and the change from protic to aprotic dipolar solvents usually increases the rate of reaction, because the basicity of the carbanions in such a medium increases as a consequence of the absence of specific solvation. Incidentally, in certain cases the addition is also facilitated by specific solvation. For example, in solvents such as acetonitrile, carbon tetrachloride, or toluene, the chalcone does not react with nitromethane in the presence of quinine, *N*-methylephedrine, or L(−)-*N*-phenylethylamine as catalysts. However, in methanol the 1,4-adducts are formed in yields of 60–80% under the conditions of weak optical induction (optical yield 1–3%):[100]

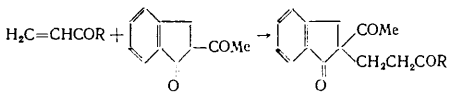
$$PhCH{=}CHCOPh + \overset{\ominus}{C}H_2NO_2 \rightarrow PhCHCH_2COPh \quad (CH_2NO_2)$$

The explanation is that in aprotic solvents chiral amines cannot ensure the generation of a carbanion from nitromethane, while in methanol this process is facilitated owing to the stabilisation of the carbanion formed as a consequence of the formation of hydrogen bonds with the solvent molecule. The use of *N*-benzylquininium fluoride or *N*-dodecylephedrinium fluoride as catalysts in toluene makes it possible to obtain the reaction products in yields of the order of 90% and with an optical yield up to 10–23%, which can most probably be attributed to the involvement of the fluoride anion in the process.[101]

Table 10. The influence of solvents on the mode of addition of 1,3-dithiane to enals.[37]

Enal	Content of adducts, %			
	in THF	in THF + HMP	in THF	in THF + HMP
	Addition to C=C		Addition to C=C	
MeCH=CHCHO	35	95	65	5
PhCH=CHCHO	15	65	85	35
H_2C=C(Me)CHO	35	95	65	5
Me_2C=CHCHO	0	35	100	65

There is no doubt that the structure of the enone and the carbanion plays a major role. Thus methyl vinyl ketone readily reacts with the carbanion generated from 1-nitro-1-*p*-tolylsulphonyloxymethane, 2-acetyl-2,3-dihydro-1-indanone, or 2-acetyl-2-[2-acetyl(or formyl)ethyl]-2,3-dihydro-1-indanone in the presence of quinine to form 1,4-adducts in high yields (87–93%) and with a high optical activity (optical yield up to 56%)[101] both in toluene and in carbon tetrachloride. Acrolein and crotonaldehyde react analogously:



Addition in the 1,4-positions also takes place in reactions with the carbanions generated from methyl 2-methylacetoacetate, ethyl 2-phenylcyanoacetate, and 2-ethoxycarbonylcyclopentanone; however, the carbanion obtained from 2-acetylcyclopentanone does not react with enones and enals under these conditions.[101]

The influence of solvation is strikingly manifested in the reaction between the trimethylsilyl ether of benzaldehyde cyanohydrin and mesityl oxide.[38] A mixture of products of addition to both the C=C and C=O bonds is formed rapidly and irreversibly in THF or DME and also in a mixture of these solvents under the conditions of kinetic control. On the other hand, when the reaction is carried out in ether, also under kinetic control, only the addition to the C=C bond is observed:

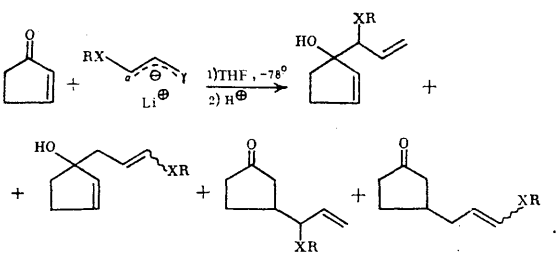
$$Me_2C{=}CHCOMe + Ph\overset{\ominus}{C}(CN)OSiMe_3\ Li^{\oplus} \rightarrow$$
$$\rightarrow Me_2C{=}CH{-}\underset{\displaystyle OH}{\underset{|}{C}}(CN)(OSiMe_3)Ph + Me_2CCH_2COMe \quad (PhC(CN)OSiMe_3)$$

When 1,3-dithiane reacts with enals, a shift towards an increase of the yield of the 1,4-adducts is observed on passing from THF to its mixture with HMP (Table 10).

Thus the above data show that polar solvents frequently promote the addition to the C=C bond.

The influence of solvation of the proportions of the 1,2- and 1,4-adducts has been studied in detail for the following nucleophiles: $(MeCH{=}CH)\overset{\ominus}{C}(CN)OCHMeOEtLi^{\oplus}$, $Ph\overset{\ominus}{C}(SR)S.(O)R^1Li^{\oplus}$, $(EtS)_2\overset{\ominus}{C}CO_2MeLi^{\oplus}$, and $H\overset{\ominus}{C}(CN)P(O)(OEt)_2Li^{\oplus}$. It has been established that, when the counterion is a lithium ion, then in THF or DME at −55 °C the above carbanions exist in the form of solvate-separated ion pairs. On the other hand, in ether, which solvates lithium ions only slightly, the same carbanions exist in the form of close (contact) ion pairs.[102–106] In the first case, the carbanion interacts only weakly with the counterion (lithium), so that a complex is formed between the lithium and the oxygen of the carbonyl group. The complex formation increases the electrophilicity of the carbonyl group by increasing the charge on the C(2) atom and by decreasing the energy level of the π^*(C=O) LUMO, which favours attack by the nucleophile on the C(1) atom.[57] In the second case the nucleophile interacts strongly with the counterion (lithium) and the latter, which interacts only weakly with the oxygen of the carbonyl group, forms an associated species. Ion pair association reduces the nucleophilicity of the carbanion as a result of the decrease of the charge on the nucleophile and the decrease of the energy level of its HOMO, which promotes the attack by nucleophiles on the C(3) atom.[57] The reversal of the direction of reaction when THF (or DME) is replaced by ether in the interaction of mesityl oxide with the carbanion generated from the trimethylsilyl ether of benzaldehyde cyanohydrin by treatment with n-BuLi can be explained by the fact that the solvate-separated ion pairs $Ph\overset{\ominus}{C}(CN)(OSiMe_3)\,||Li^{\oplus}$ are then converted into the close ion pairs $[Ph\overset{\ominus}{C}(CN)(OSiMe_3)][Li^{\oplus}]$,[73,106] which is accompanied by a decrease of the negative charge on the carbanionic centre and is responsible for the preferential attack on the C(3) atom despite some decrease of the energy of the HOMO of the nucleophile.

An interesting example of the change of direction of the reaction as the solvent composition is altered is provided by the reaction of cyclopent-2-enone with the carbanion generated by treating $RXCH_2CH{=}CH_2$ with n-BuLi at −78 °C.[107] In THF the reaction proceeds in accordance with the mechanism



This results in the formation of mainly a mixture of the α- and γ-1,2-adducts. The addition of only one mole of HMP results in a sharp change in regioselectivity and mainly the α-1,4-adduct is obtained (Table 11). We may note that a decrease of the amount of added HMP leads to the appearance of α- and γ-1,2-adducts in the mixture. A complete inversion of the direction of reaction in this instance can probably be accounted for by the fact that the effective solvation of lithium ions increases the energy of the HOMO of the nucleophile and leads to orbital control, which promotes 1,4-addition.[107-110] The change in the regioselectivity of the addition of CH acids to enals and enones by the addition of HMP is nowadays already used fairly widely in organic synthesis, for example, in the synthesis of α,α,β-trisubstituted ketones and natural products (confertin, aromatin, etc.).[111]

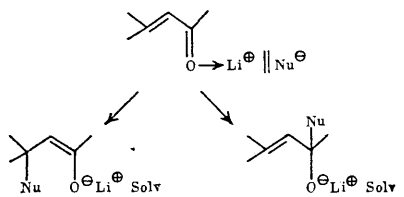
Table 11. The influence of the nature of solvents on the composition of the products of the reaction of cyclopent-2-enone with $RXCH_2CH = CH_2$ (according to the data of Binus and Haynes[107]).

R	X	Solvent	Composition of reaction products, %				Overall yield, %
			α-1,2	γ-1,2	α-1,4	γ-1,4	
Ph	S	THF	60	18(1.0:1.1)	12	8(1.0:4.2)	85
Ph	S	THF + HMP**	0	0	95	5	89
Ph_3C	S	THF	30	70	—	—	30
Ph_3C	S	THF + HMP**	0	0	90	10	30
Me	S	THF	64	36(1.0:0.6)	0	0	87
Me	S	THF + HMP**	0	0	95	5	89
t-Bu	S	THF	42	58(1.00:0.25)	0	0	85
t-Bu	S	THF + HMP**	0	0	95	5	85
Ph	Se	THF	58	20	12	10(1.0:1.9)	79
Ph	Se	THF + HMP**	0	0	95	5	81

*The ratio of the *Z*- and *E*-isomers is given in brackets.
**One mole of HMP was added.

Additives and the Mode of Reaction

It has been established in recent years that the introduction of certain additives into the reaction mixture makes it possible, by the change of solvent, to alter the regioselectivity of the addition of CH acids to enals and enones. Table 12 illustrates, for example, the influence of additives on the ratio of 1,2- and 1,4-adducts in the reaction of mesityl oxide with the trimethylsilyl ether of benzaldehyde cyanohydrin in the presence of n-BuLi.[73] Evidently, the addition of 12- crown-4 ether, which fully displaces the reaction towards 1,2-addition in DME and even in ether leads to the formation of 76% of the products of addition to the C=O bond, evidently exerts the greatest influence. This is undoubtedly associated with the formation of stable complexes between 12-crown-4 ether and lithium ions[112,113] (see the previous Section). The addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and lithium bromide and perchlorate hardly alters the mode of reaction but the introduction of magnesium bromide increases the content of the 1,4-adducts in the mixture. It may be that a complex is formed in this case between the solvated nucleophile ion pair and the enone via the carbonyl group and is capable of ensuring both reaction pathways, involving the 1,2- and 1,4-positions:



The slight tendency towards an increase of the content of the 1,4-adducts (from 22 to 26–28%) following the addition of lithium salts is also probably associated with the analogous complex formation reaction.

Table 12.

Solvent	Additive	Compn. of reaction products, %		Overall yield, %
		via C=O bond	via C=C bond	
DME	—	78	22	98
DME	TMEDA*	80	20	98
DME	12-crown-4 ether*	100	0	88
Ether	12-crown-4 ether*	76	24	90
DME	LiBr**	72	28	91
DME	$LiClO_4$**	74	26	91
THF	$MgBr_2$***	42	58	97

*One mole in relation to the substrate was added.
**Saturated solutions in a 2:1 DME–hexane mixture.
***0.5 of a mole in relation to the substrate was added.

It is noteworthy that the reaction of the t-butylthioallyl anion with cyclopent-2-enone in THF in the presence of three moles of TMEDA leads to an 80% yield of only a mixture of the α-1,2-isomer (41%) and the γ-1,2-isomer (59%), while the addition of copper(I) iodide entails the formation of the 1,4-adduct alone in a 75% yield.[107] The complete shift towards 1,4-addition in the reaction of ethyl propionate with 2-phenylthiocyclopent-2-enone in THF at −78 °C was induced by the addition of a complex of copper iodide with trimethyl phosphite.[111] This resulted in the formation of 2-phenylthio-3-(1-ethoxycarbonylethyl)cyclopentanone in a 64% yield as a mixture of four diastereoisomers in proportions of 18:2:9:71. In the absence of the additive, only the 1,2-adduct was formed, namely 1-hydroxy-1-(1-ethoxycarbonylethyl)-2-phenylthiocyclopent-2-ene.[111]

Finally, mention should be made of the effect of yet another factor on the mode of reaction, namely the pressure. It has been shown that the addition of ethyl- and n-butylmalonic esters to the C=C bond of the chalcone does not take place at atmospheric pressure. However, an increase of the pressure to 10–15 kbar makes it possible to obtain the products of the Michael addition in yields of 70–95%.[114-116]

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By virtue of the advances achieved in the study of the nucleophilic addition of CH acids of the type of XCH_2Y and XYCHZ to enones and enals, it has now become possible to achieve the regioselective addition in the 1,2- and 1,4-positions by selecting the appropriate nucleophiles, enones and enals, bases for the generation of the carbanions, solvents, and additives. 1,2-Addition is favoured by selecting nucleophiles with the charge most highly localised on the nucleophilic centre (CH acids with low pK_a), the use of enones and enals with sterically hindered C(3) atoms or with electron-donating substituents in the 3-position, the use of bases whose cations form complexes with the oxygen of the carbonyl group most readily, and the application of solvents promoting the formation of solvate-separated ion pairs comprising the carbanion and the counterion (the base cation) as well as additives forming complexes with the cations.

1,4-Addition is promoted by selecting nucleophiles with the most delocalised charge (CH acids with high pK_a), the employment of enones and enals without substituents giving rise to steric hindrance at the C(3) atom, and the application of bases whose cations are poor complex forming agents in relation to the oxygen atom of the carbonyl group and solvents promoting the formation of close ion pairs between the carbanion and the counterions.

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Zelinskii Institute of Organic Chemistry,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 1304-1324 (1984) U.D.C. 547.834

Advances in the Chemistry of α, α, α′, α′-Tetrasubstituted Piperidines

L.N.Yakhontov

The stages in the development of the chemistry of piperidines with a sterically hindered nitrogen atom and the practical importance of compounds of this class are examined. The methods of synthesis of 2,2,6,6-tetra-alkylpiperidines published in the literature, and their chemical properties and reactions are surveyed: processes occurring without the growth of a carbon skeleton, condensations with the formation of new C-C bonds, and reactions involving a change in the heterocyclic skeleton of the molecules. The characteristics of the stereochemistry and in particular of the conformations of 2,2,6,6-tetrasubstituted piperidines are analysed.
The bibliography includes 174 references.

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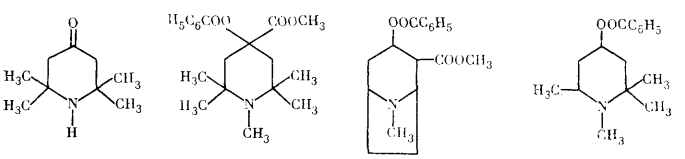
I. INTRODUCTION

The introduction of various kinds of substituents into the α- and α′-positions relative to the nitrogen atom in N-heterocyclic systems leads to a significant alteration of the chemical properties of the compounds. Effects of this kind were examined in our previous study[1] for N-heteroaromatic substances in relation to 2,6-disubstituted pyridines.

In contrast to heteroaromatic derivatives, where various electromeric effects (both effects transmittable via the bonds and "shield effects"), play an important role, steric effects associated with the shielding of the heterocyclic nitrogen atom are of primary importance for heteroparaffins of the type of α,α,α′,α′(2,2,6,6)-tetrasubstituted piperidine. Unfortunately the number of theoretical studies on this problem is inadequate and the reviews devoted to the synthesis and chemical reactions of 2,2,6,6-tetrasubstituted piperidines are altogether lacking. The thorough review articles and monographs on iminoxy-radicals of the type of 2,2,6,6-tetramethylpiperidin-1-yloxy-radical are the only exception.[2-17]

II. STAGES IN THE DEVELOPMENT OF THE CHEMISTRY OF α,α,α′,α′-TETRASUBSTITUTED PIPERIDINES

Studies on 2,2,6,6-tetrasubstituted piperidines having a hindered heterocyclic nitrogen atom were begun more than a hundred years ago when triacetoneamine was isolated from the products of the interaction of acetone with ammonia and its structure was established as 2,2,6,6-tetramethyl-4-piperidinone (I).[18,19] For a long time, the study of compounds of this series reduced to the synthesis of derivatives of compound (I) involving the carbonyl group and the nitrogen of the piperidine ring. Data on the local anaesthetic activity of α-eucaine (II), a derivative of 1,2,2,6,6-pentamethylpiperidine which is a cheaper, less toxic, and more heat resistant analogue of cocaine (III), were published in the only communication on the biological properties of substances of this type.[20] However, in view of the intense local irritant action of compound (II), it was soon eliminated from medical practice by β-eucaine (IV), which is free from this disadvantage:

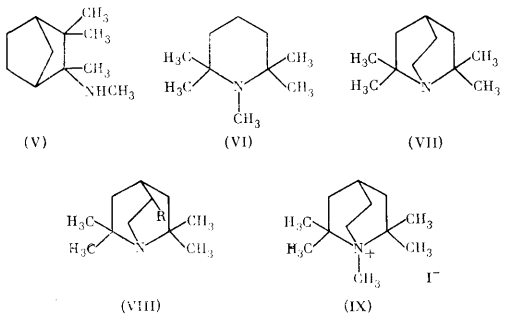


(I) (II) (III) (IV)

A new stage in the study of 2,2,6,6-tetrasubstituted piperidines was begun in the 1950's in connection with the search for ganglion-blocking agents. By that time it had been established that, in contrast to the ganglion-blocking quaternary ammonium compounds widely used in medical practice but poorly assimilated from the gastrointestinal tract and secondary amines with a hindered nitrogen atom of the type of camphonium (V), which exert a secondary central activity (depression of the central nervous system, tremor), 2,2,6,6-tetramethylpiperidines unsubstituted in the 1-position and 1-alkyl-2,2,6,6-tetramethylpiperidines, which exhibit an intense ganglion-blocking activity, are rapidly assimilated following peroral administration and are free from side effects on the central nervous system.[21] Among compounds of this group, the most active proved to be 1,2,2,6,6-pentamethylpiperidine (VI) which has been introduced into medical practice under the names pempidine, pyrilene, genoriol, perolysen, etc. and is still used as an effective ganglion-blocking agent.[22-24]

The study of numerous analogues of compound (VI) [25-35] showed that steric hindrance of the nitrogen atom is a more important factor for the ganglion-blocking activity of compounds of this type than a change in the structure of the heterocycle. An increase in the bulk of the substituent at the nitrogen atom lowers the activity. The introduction of a

double bond into the ring does not affect the activity but reduces the duration of action and increases the toxicity:[27-29]



(V) (VI) (VII)

(VIII) (IX)

Ganglion-blocking and sedative properties have also been shown by triacetoneamine (I),[36-38] which has been given the name tempidone in Bulgaria. Further studies designed to search for ganglion-blocking agents more active than pyrilene led to the development of new methods of synthesis of 2,2,6,6-tetramethylpyridines[28,39-41] and then to the synthesis of the quinuclidine analogue of compound (VI)—the medicinal drug temekhin (VII).[42] The latter exhibits an activity which is three times more selective than that of pyrilene (VI) in relation to muscarinic cholinoceptor autonomic ganglia, the cortical substance of suprarenal glands, and carotid body without influencing the nicotinic cholinoceptor system of skeletal muscles. Temekhin is characterised by a broad spectrum of its therapeutic activity, is manufactured by the chemical-pharmaceutical industry of the USSR, and is used in medicine as a ganglion-blocking and hypotensive agent.[43] The additional introduction of the 8-methyl-group into the temeckin molecule to give compound (VIII, R = CH_3) increased somewhat the toxicity of the preparation with retention of its activity. The increase in the length of the 8-alkyl chain or conversion into 8-substituted functional derivatives (VII) leads to a further increase of toxicity with the simultaneous reduction of the ganglion-blocking effect.[44-46] The activity of the preparation changes in another direction on quaternisation as the bridgehead nitrogen atom. 2,2,6,6-Tetramethylquinuclidine methiodide (IX), which has been called imequine,[47] is also manufactured by the chemical-pharmaceutical industry of the USSR and is used in medical practice for the creation of artificial hypotonia in surgical operations, in the treatment of the oedemas of the lungs and the brain and the chronic hypotonia associated with kidney failure, and for the prevention and arrest of hypertonic crises. In all cases imequine behaves as a drug which is stronger, more easily controlled, less toxic, and more convenient for practical use than a preparation having a different chemical structure (arfonad) used for such purposes outside the USSR.[43]

The organisation of the manufacture of initially pyrilene and then temekhin and imequine, whose synthesis is based on the use of triacetoneamine(I), created a realistic industrial raw material base for the preparation of various derivatives of 2,2,6,6-tetramethylpiperidine.

A new stimulus to the development of the chemistry of 2,2,6,6-tetrasubstituted piperidines was provided by studies and practical employment of iminoxy-radicals.[2-17] 2,2,6,6-Tetramethyl-4-oxopiperidine 1-oxide (X), which is an iminoxy-radical based on triacetoneamine whose stability is due to steric factors, was first obtained in a pure form in 1962.[48] This was followed by numerous studies of various methods of synthesis of 2,2,6,6-tetramethylpiperidin-1-yloxy-radicals and their reactions involving the participation of both the free-radical function and others in which the unpaired electron does not participate. Iminoxy-radicals of the 2,2,6,6-tetramethylpiperidine series are widely used in the solution of many theoretical and applied problems in experimental biophysics, the chemistry of high-molecular-weight compounds, analytical and forensic chemistry, biochemistry, and molecular biology (as spin labels and probes, paramagnetic inhibitors, and stabilisers), in instrument making (lasers and masers, current sources, magnetometers, and dosimeters), etc. The availability of fairly careful reviews and monographs on the chemistry and applications of paramagnetic 2,2,6,6-tetrasubstituted piperidin-1-yloxy-radicals[2-17] makes it possible to restrict the present review to the consideration of mainly only diamagnetic 2,2,6,6-tetrasubstituted piperidines, which are used in many instances as the starting materials for the synthesis of stable iminoxy-radicals.

At the present stage of development of the chemistry of 2,2,6,6-tetrasubstituted piperidines, a fairly vigorous development of all the trends established in this field as a result of historical factors has continued. The study of the theoretical and preparative problems of the chemistry of 2,2,6,6-tetrasubstituted piperidines has been concentrated in recent years on the elucidation of the characteristics of the conformation of sterically hindered piperidines, the determination of the contribution of axial and equatorial α-methyl groups to the stereochemistry of other substituents,[49-51] the ionisation potentials of the photochemical reactions of the test substances,[52-54] etc.

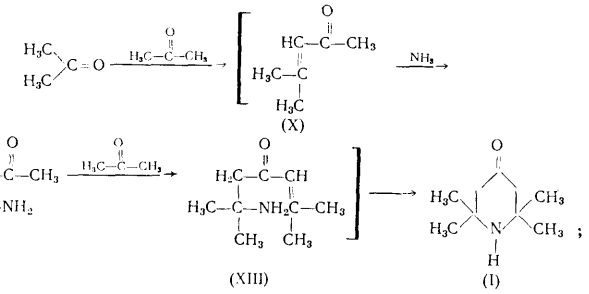
Together with the extensive studies on nitroxy-radicals, 2,2,6,6-tetramethylpiperidine-1-thiyl radicals,[55] 2,2,6,6-tetramethylpiperidine-1-nitrenes,[56] and 2,2,6,6-tetramethylpiperidin-1-yl radicals[57] have been obtained and have aroused interest.

Vigorous search for new biologically active 2,2,6,6-tetrasubstituted piperidines[53,54,58-66] is being continued and studies on the employment of compounds of this class for the formation of polymeric materials are developing.[67-72]

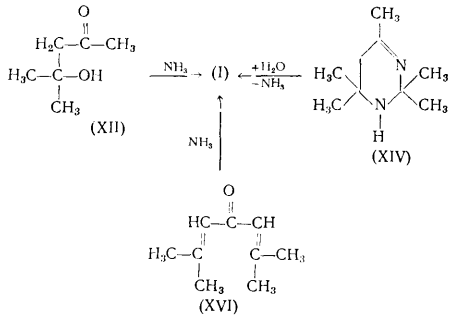
III. METHODS OF SYNTHESIS OF α,α,α′,α′-TETRASUBSTITUTED PIPERIDINE SYSTEMS

In considering the methods for the closure of 2,2,6,6-tetrasubstituted piperidine rings developed hitherto, one should note that attention has been concentrated on the synthesis of 2,2,6,6-tetramethyl-4-piperidinone (triacetoneamine). The vast majority of 2,2,6,6-tetrasubstituted piperidines known at present have been synthesised from triacetoneamine. According to the method[18] for the synthesis of compound (I) developed as early as 1874, ammonia was passed into acetone with heating.[19,73] Subsequently the process was carried out at room temperature and calcium chloride was added to the reaction mass to improve the absorption of ammonia and to bind the water formed during the reaction.[74-76] Different versions of this process have been developed: with the ammonia passed in several portions into a mixture of acetone and calcium chloride taking into account the amount of ammonia[40,77] and with subsequent maintenance of the reaction mass at 20 °C for 4 days[28,40,78] or with boiling it in the course of 6 h.[79] A special apparatus has been proposed for the reaction providing for the periodic separation of the calcium chloride solution[80,81] and it has been demonstrated that many protic and Lewis acids exert a catalytic influence on this process.[82-84] The application in this reaction of liquefied ammonia of the ammine complex of calcium chloride prepared beforehand has been described.[85] However, in all cases the reaction does not proceed unambiguously[78] and the yield of triacetoneamine relative to the acetone employed is about 30%.

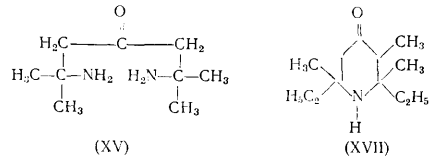
The interaction of acetone with ammonia apparently proceeds via the formation of mesityl oxide (X) and diacetoneamine (XI),[86] compound (XI) being the main reaction product at room temperature.[87] Diacetone alcohol (XII),[77] diacetonamine,[74,77,88] mesityl oxide,[77] acetonin (2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine) (XIV),[77,78,87,89] triacetonediamine (XV),[90] etc. have been detected as side products in the synthesis of triacetoneamine.



(X) (XI) (XIII) (I)



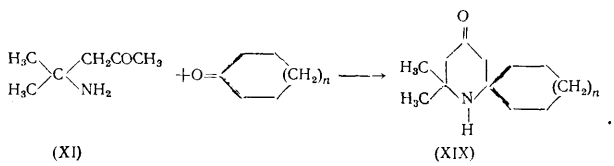
(XII) (XIV) (XVI)



(XV) (XVII)

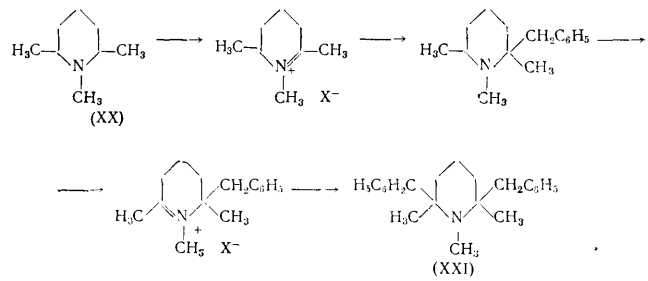
Triacetoneamine can also be obtained from phorone (XVI) and ammonia,[73,91,92] from acetonin (XIV) and water in the presence of calcium chloride,[78] and from diacetone alcohol (XII) by catalytic condensation with ammonia.[78] Despite the fact that the yields of triacetoneamine in the above reactions are somewhat higher (from 48 to 68%), the lower availability of the starting materials precludes preference being given to these procedures in the synthesis of compound (I) compared with the classical method involving the condensation of acetone with ammonia.

An analogous condensation of ethyl methyl ketone with ammonia has been used to synthesise 2,6-diethyl-2,3,6-trimethyl-4-piperidinone (XVII).[93] When diacetoneamine was allowed to react with cyclopentanone (XVIII, $n = 0$) and cyclohexanone (XVIII, $n = 1$), compounds (XIX, $n = 0$ and 1) were synthesised in yields of 20 and 54% respectively:[78]



(XI) (XIX)

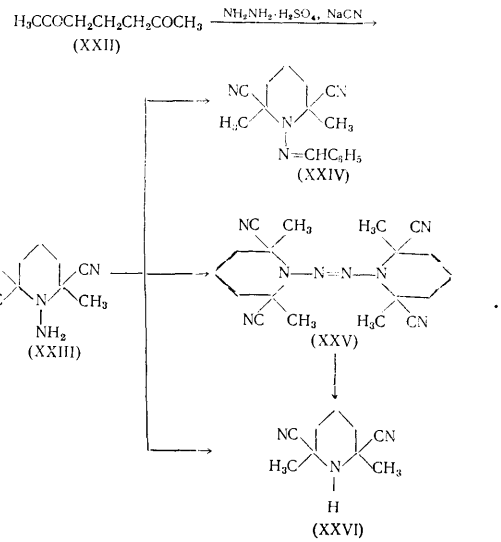
A novel method for the conversion of 1,2,6-trimethylpiperidine (XX) into 2,6-dibenzyl-1,2,6-trimethylpiperidine (XXI) consists in a twofold repetition of the reactions involving the oxidation of the piperidine derivative by mercury acetate to the corresponding Δ'-dehydro-derivatives in yields of the order of 66–67% and subsequent addition of benzylmagnesium bromide to the double bond in yields of 95–96% in accordance with the scheme[94]



(XX) (XXI)

Unfortunately analogous reactions using alkylmagnesium halides failed to yield satisfactory results.[94]

The reaction of heptane-2,6-dione (XXII) with hydrazine sulphate and sodium cyanide, which results in the formation of 1-amino-2,6-dicyano-2,6-dimethylpiperidine (XXIII), has been described. The latter reacts with benzaldehyde to form the benzylidene derivative (XXIV) and, on oxidation with potassium permanganate, it is converted into the tetrazine (XXV). The cleavage of the tetrazene with hydrobromic acid and treatment of the *N*-amino-compound (XXIII) with sodium nitrite in an acid medium led to 2,6-dicyano-2,6-dimethylpiperidine (XXVI):[95]



(XXII) (XXIV) (XXIII) (XXV) (XXVI)

IV. CHEMICAL REACTIONS OF α,α,α',α'-TETRASUBSTITUTED PIPERIDINES

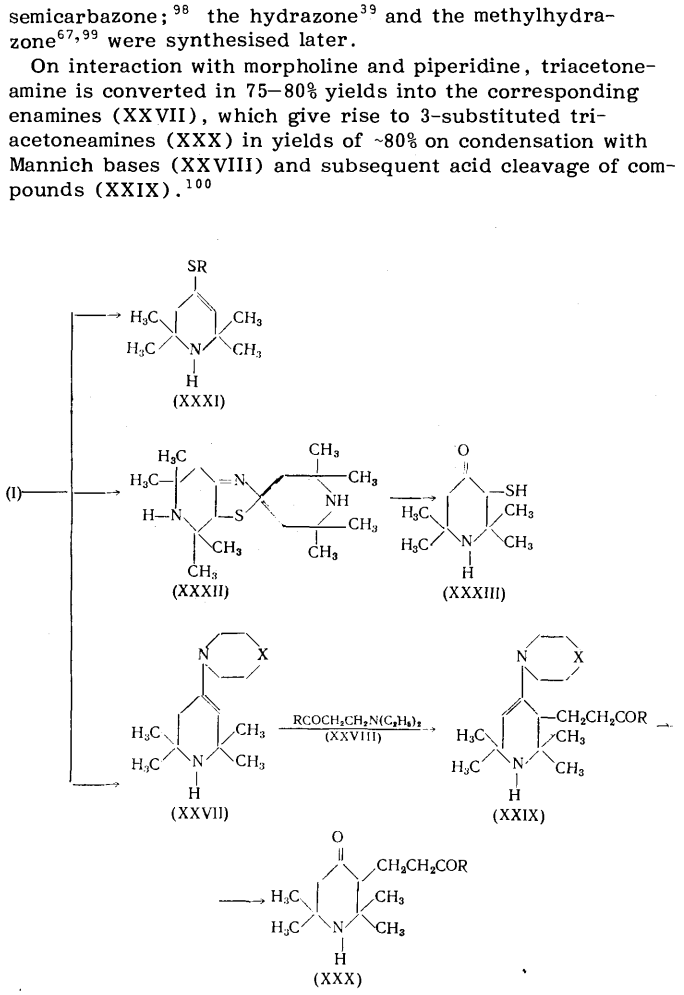
The comprehensive study of the reactivity of triacetoneamine has been important for the development of the chemistry of 2,2,6,6-tetrasubstituted piperidines.

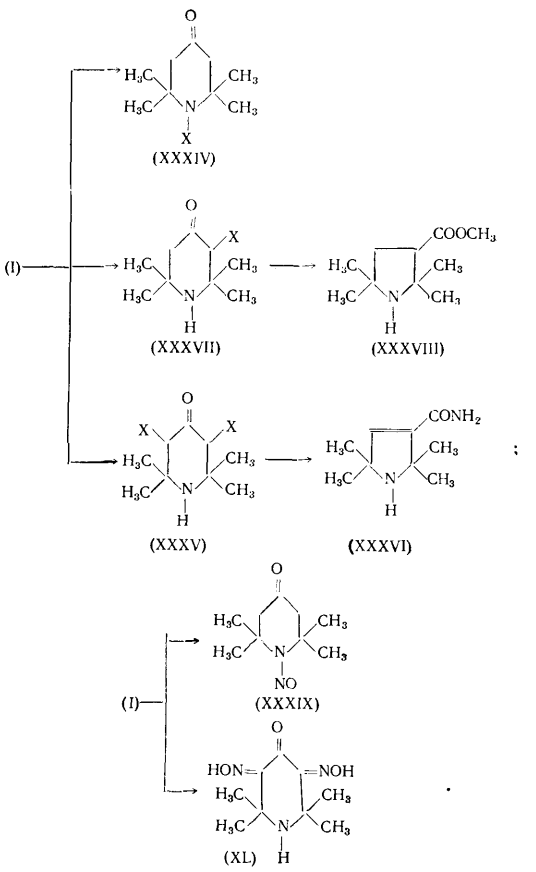
1. Reactions without the Growth of the Carbon Skeleton

Typical derivatives involving the carbonyl group of compound (I) were obtained already in the early stages of the investigation: the oxime,[96] the phenylhydrazone,[97] the

semicarbazone;[98] the hydrazone[39] and the methylhydrazone[67,99] were synthesised later.

On interaction with morpholine and piperidine, triacetoneamine is converted in 75–80% yields into the corresponding enamines (XXVII), which give rise to 3-substituted triacetoneamines (XXX) in yields of ~80% on condensation with Mannich bases (XXVIII) and subsequent acid cleavage of compounds (XXIX).[100]





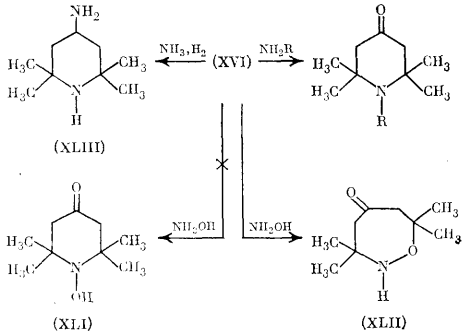
Compound (I) reacts with ethanethiol and thiophenol in an alcoholic hydrochloric acid solution and is converted into *S*-substituted 4-mercapto-2,2,6,6-tetramethyltetrahydropyridines (XXXI),[101] while the interaction with sulphur and ammonia gives rise to 5,5,7,7-tetramethyl-1,2,5,6,7,7a-hexahydrothiazolo[5,4-*c*]pyridine-2,4-spiro-4-(2′,2′,6′,6′-tetramethylpiperidine) (XXXII), which readily hydrolyses to 3-mercapto-2,2,6,6-tetramethyl-4-piperidinone (XXXIII).[80]

Compound (I) reacts with halogens in polar media to form the *N*-halogeno-derivative (XXXIV)[101–103] or, under more severe conditions, 3,5-dihalogeno-derivatives (XXXV), where X = Cl or Br.[91,102] On treatment with ammonia, the latter undergo ring contraction with formation of 2,2,5,5-tetramethyl-2,5-dihydropyrrole-3-carboxamide (XXXVI).[91] In non-polar media, the halogenation of compound (I) makes it possible to obtain the 3-monohalogeno-derivatives (XXXVII, X = Cl or Br), which react with sodium methoxide to give the methyl ester of 2,2,5,5-tetramethylpyrrolidine-3-carboxylic acid (XXXVIII) as a result of ring contraction.[104] In acetonitrile or aqueous methanol, compound (I) reacts with $FClO_3$ to form the *N*-fluoro-derivative (XXXIV, X = F) and the reaction is of first order with respect to each reactant.[105] Depending on the reaction conditions, the nitrosation of compound (I) can proceed with formation of the *N*-nitroso-derivative (XXXIX)[106] or the derivatives (XL) substituted in the 3,5-positions.

The *N*-halogenation[107] and *N*-nitrosation processes[56,57,108] have been used also in the case of other 2,2,6,6-tetrasubstituted piperidines. 1-Chloro-2,2,6,6-tetramethylpiperidine has found an application as a chlorinating agent.[107]

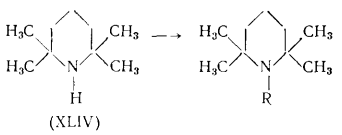
1,2,2,6,6-Pentamethyl-4-piperidinone has been obtained by methylating triacetoneamine with methyl iodide. However, a more convenient and more general method for the introduction of the *N*-methyl group into 2,2,6,6-tetramethylpiperidine derivatives proved to involve their treatment with a mixture of formaldehyde and formic acid.[39,40,109,110] In order to obtain compounds with more bulky substituents at the nitrogen atom, derivatives of 2,2,6,6-tetramethylpiperidine are treated with the corresponding halogen-containing compounds or epoxyethane derivatives.[27,41,64,111–116]

Another version of the synthesis of *N*-alkyl- and *N*-arylalkyl-2,2,6,6-tetramethylpiperidines involves the interaction of the corresponding primary amines with phorone.[73] It is noteworthy that the analogous reaction of phorone with hydroxylamine does not lead to 1-hydroxytriacetoneamine (XLI), as described previously,[90] but to hexahydro-3,3,7,7-tetramethyl-1,2-oxazepin-5-one (XLII).[117] 4-Amino-2,2,6,6-tetramethylpiperidine (XLIII) has been obtained by the reductive ammination of phorone with ammonia and hydrogen at 110–150 °C and 100–180 atm in the presence of various catalysts:[118]



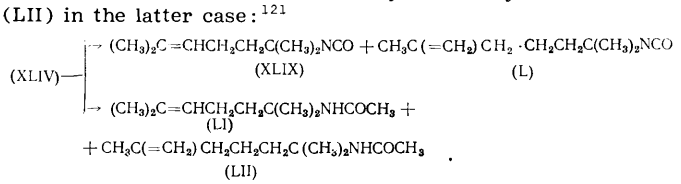
(XLI) (XLII)

On reaction with butyl-lithium and subsequent treatment with alkyl halides, 2,2,6,6-tetramethyl-1-propynylpiperidine (XLV), synthesised by alkylating 2,2,6,6-tetramethylpiperidine (XLIV), was converted into the αβ-ynamino-derivative (XLVI) which gives rise to the corresponding amides (XLVII) on hydration:[119]

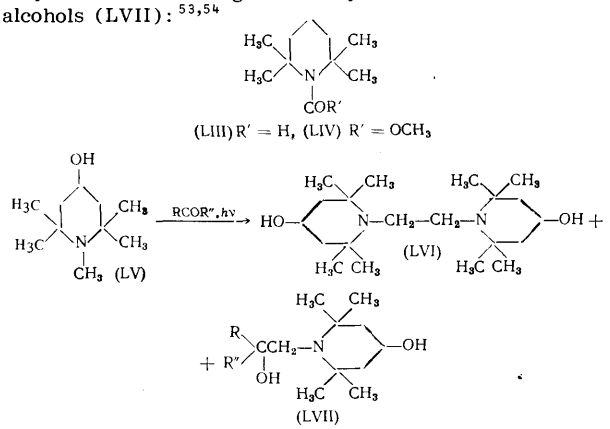


(XLV) R = C≡CCH$_3$,
(XLVI) R = C≡CCH$_2$R',
(XLVII) R = COCH$_2$R',
(XLVIII) R = COC$_6$H$_5$.

The *N*-benzoyl derivative (XLVIII) has been obtained by the reaction of compound (XLIV) with benzoyl chloride in benzene in 55% yield.[120,121] However, the reaction with phosgene and acetyl chloride resulted in the opening of the piperidine ring with formation of 1,1,5-trimethylhex-4-enyl isocyanate (XLIX) and 1,1,5-trimethylhex-5-enyl isocyanate (L) in the former case and *N*-(1,1,5-trimethylhex-4-enyl)-acetamine (LI) and *N*-(1,1,5-trimethylhex-5-enyl)acetamide (LII) in the latter case:[121]



1-Methoxycarbonyl-2,2,6,6-tetramethylpiperidine (LIV) has been obtained by the electrochemical oxidation of 1-formyl-2,2,6,6-tetramethylpiperidine (LIII) in methanol at a platinum anode,[122] while in the photochemical oxidation of 1,2,2,6,6,-pentamethyl-4-piperidinol (LV) by ketones the process involves the *N*-methyl group with formation of the dimeric product (LVI) and 2,2,6,6-tetramethyl-4-piperidinols alkylated at the nitrogen atom by the residues of the tertiary alcohols (LVII):[53,54]

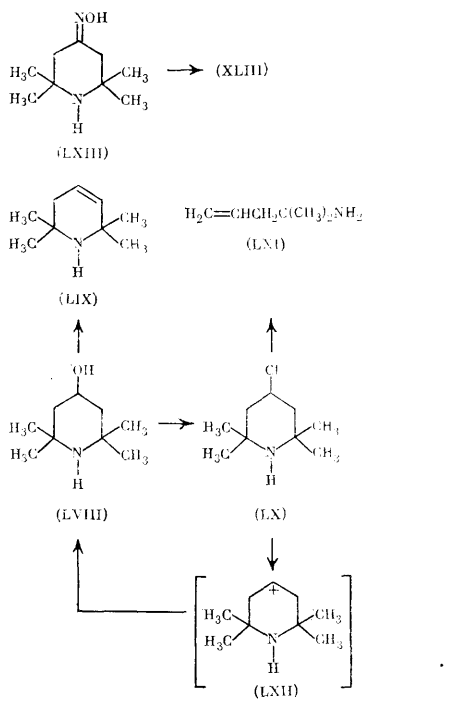


(LIII) R' = H, (LIV) R' = OCH$_3$

(LV) (LVI) (LVII)

The oxo-group is usually eliminated from the 4-position of triacetoneamine and other 2,2,6,6-tetramethyl-4-piperidinones by the Wolff–Kishner reduction with hydrazine hydrate and potassium hydroxide in triethylene glycol,[76,120] ethylene glycol,[40] or glycerol[28] in 50–70% yields. In the reactions with sodium tetrahydroborate,[93] lithium tetrahdyroaluminate,[109] sodium in alcohol, sodium amalgam,[93] and hydrogen in the presence of a nickel catalyst[109] or in the electrochemical reduction,[123] the products are, as was to be expected, the corresponding 2,2,6,6-tetramethyl-4-piperidinols. Under these conditions, the alcohol (LVIII), with the equatorial disposition of the hydroxy-group and the chair configuration of the heterocycle, was obtained from triacetoneamine.[124] On treatment with thionyl chloride, the above alcohol is readily converted into the dehydropiperidine derivative (LIX), but, on reaction with hydrochloric acid, compound (LVIII) gives rise to 4-chloro-2,2,6,6-tetramethylpiperidine (LX).[125] On alkaline hydrolysis, the chloride (LX) undergoes synchronous fragmentation with formation of 2-amino-2-methylpent-4-ene (LXI) and is simultaneously converted at a lower rate into 2,2,6,6-tetramethyl-4-piperidinol via the carbonium ion (LXII)[126] (see the Scheme below).

Scheme

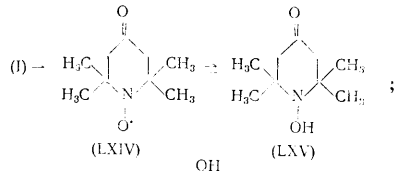


(LXIII) (LIX) (LXI) (LVIII) (LX) (LXII)

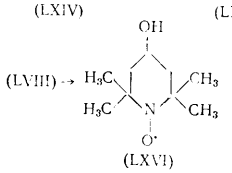
In order to investigate the spasmolytic and antiviral activities, the esters of the alcohol (LVIII) were obtained[127,128] and were used to synthesise the guanidine derivatives.[39] The reduction of the oxime of triacetoneamine (LXIII), both catalytic and with lithium tetrahydroaluminate, yielded 4-amino-2,2,6,6-tetramethylpiperidine.[39]

Cautious oxidation of triacetoneamine with hydrogen peroxide in the presence of catalysts (tungsten, molybdenum, or vanadium salts) leads to the stable iminoxy-radical (LXIV),[48] which forms an oxime, a semicarbazone, and a 2,4-dinitrophenylhydrazone,[48] undergoes the Wolff–Kishner reduction[129] and the Beckmann rearrangement,[130,131] enters into a modified Wittig reaction,[132] and gives rise to a spirohydantoin derivative[133] without involving the centre where the unpaired electron is localised. At the same time the catalytic

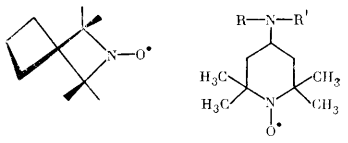
reduction of compound (LXIV) in the presence of palladium leads to a diamagnetic substance—1-hydroxytriacetoneamine (LXV).[48] Fermi's salt (potassium nitrosodisulphonate) is used to convert the *N*-hydroxy-compounds (LXV) into the iminoxy-radical (LXIV):[134]



(LXIV) (LXV)

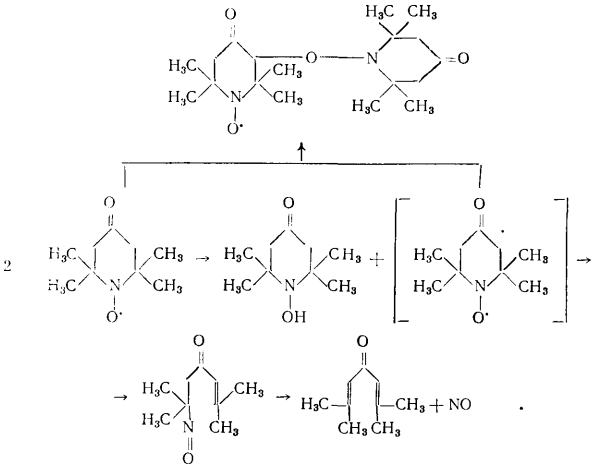


(LXVI)



(LXVII) (LXVIII)

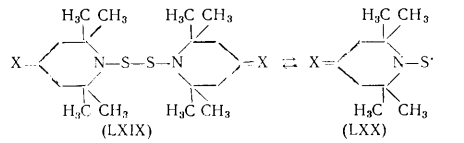
The corresponding 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-radical (LXVI) has been obtained by oxidising compound (LVIII) with hydrogen peroxide.[135] The use of peracids for the same purpose involves simultaneously the 4-hydroxy-group, converting it into the oxo-group.[136] The 2,2,6,6-tetramethyl-4-oxo-piperidin-1-yloxy-radical (LXIV) has the symmetrical twist-conformation (LXVII) in the solid state,[137] while in the gas phase[138] and in solution[139] the nitrogen atom is at the apex of the pyramid. The relative instability of compound (LXIV) is associated with the activation of the hydrogen atoms in the 3- and 5-positions adjoining the carbonyl group, which leads to a slow disproportionation of the radical in accordance with the scheme[140]



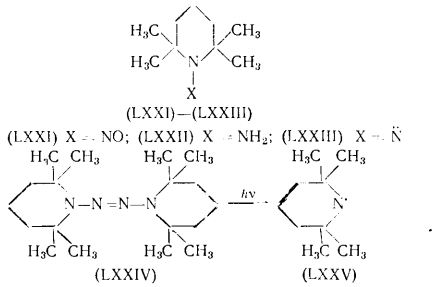
The iminoxy-radical (LXIV) can be used for the effective binding of the benzoyl and benzyl radicals. Acylation of the iminoxy-radical (LXVI) at the hydroxy-groups proceeds without involving the radical centre.[8,135,141–145] Substituted 4-amino-2,2,6,6-tetramethylpiperidin-1-yloxy-radicals (LXVIII) have been obtained by the reductive amination of compound (LXIV) by primary and secondary amines in the presence of sodium cyanohydroborate at pH 5–9.[146–150]

The study of the mechanism of the oxidation of compound (XVIII) by cumenyl hydroperoxide showed that the rate-determining stage is the formation of the N-radical-cation, which reacts with the excess hydroperoxide and is converted into an intermediate quaternary *N*-hydroxyammonium salt, which dissociates to the iminoxy-radical.[151] Many other methods of synthesis of various stable nitroxy-radicals by the oxidation of 2,2,6,6-tetrasubstituted piperidines and via a wide variety of reactions of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yloxy-, 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy, and 4-aminopiperidin-1-yloxy-radicals without involving the *N*-oxy-group have been published in the literature. These methods have been described in detail in reviews.[2–7] Problems concerning the relation between the electronic structure of the iminoxy-radicals and their acute toxicity have been considered.[152]

Further investigations showed that compounds (I) and (XLIV) react with sulphur dichloride in dimethylformamide and are converted into the disulphides (LXIX), which dissociate on heating to 2,2,6,6-tetramethylpiperidine-1-thiyl radicals (LXX), which readily dimerise on cooling.[55] In less polar solvents (hexane, ether) the process leads towards the formation of polysulphides containing from three to five sulphur atoms.[55]



(LXIX) (LXX)



(LXXI)—(LXXIII)

(LXXI) X = NO; (LXXII) X = NH_2; (LXXIII) X = N

(LXXIV) (LXXV)

The reduction of 2,2,6,6-tetramethyl-1-nitrosopiperidine (LXXI) with lithium tetrahydroaluminate yielded 1-amino-2,2,6,6-tetramethylpiperidine (LXXII),[153] whose treatment with t-butyl hypochlorite in ether at −78 °C in the presence of triethylamine led to the formation of *N*-(2,2,6,6-tetramethylpiperidine)nitrene (LXXIII).[56] Other nitrenes of this type have been described in the literature.[154–156] The ultraviolet spectrum of compound (LXXIII), recorded at −78 °C, is characterised by an appreciable absorption due to the $n\pi^*$ transition, while the intense absorption at 1595 cm^{-1} in the infrared spectrum indicates a considerable amount of double bond character in the N–N group in the ground state. At 0 °C the nitrene (LXXIII) readily decomposes and the rate of decomposition in solutions is inversely proportional to the solvent polarity. There is a simultaneous bimolecular reaction leading to the formation of 1,1-tetrazene (LXXIV).[56] The photolysis of compound (LXXIV) generates the 2,2,6,6-tetramethylpiperidinyl radical (LXXV), which is much less stable than iminoxy-radicals. It readily splits off hydrogen from solvents and is readily oxidised by oxygen to the nitroxide {the labelled [^{17}O] nitroxide has been synthesised using $^{17}O_2$}.[57] The 2,2,6,6-tetramethyl-4-oxopiperidinyl radical, whose stability is low, has been obtained by the photolysis of *N*-bromotriacetoneamine (XXXIV, X = Br).[157]

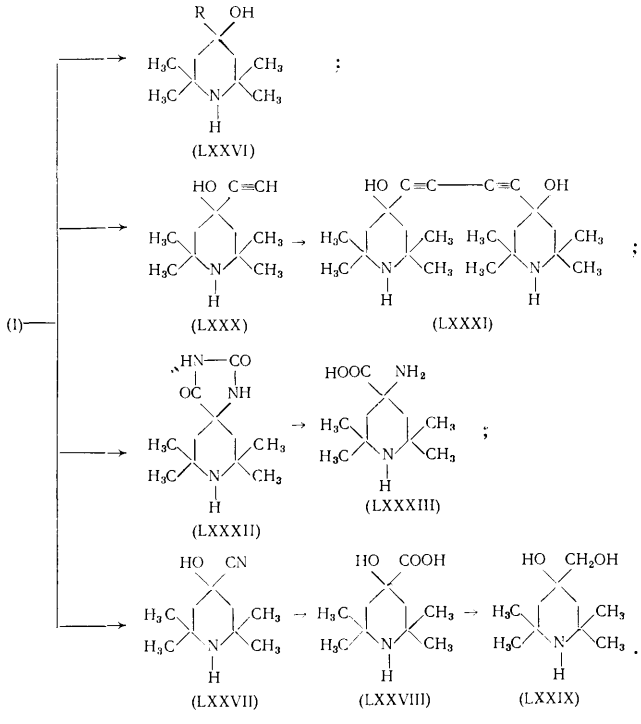
2. Reactions Involving the Formation of New C–C Bonds at the Piperidine Ring

Together with the reactions described above, which take place mainly without the growth of the carbon skeleton at the piperidine ring, processes involving the formation of new C–C bonds due to various condensations involving the heterocyclic skeleton of the molecule occupy an important place in the chemistry of 2,2,6,6-tetrasubstituted piperidines.

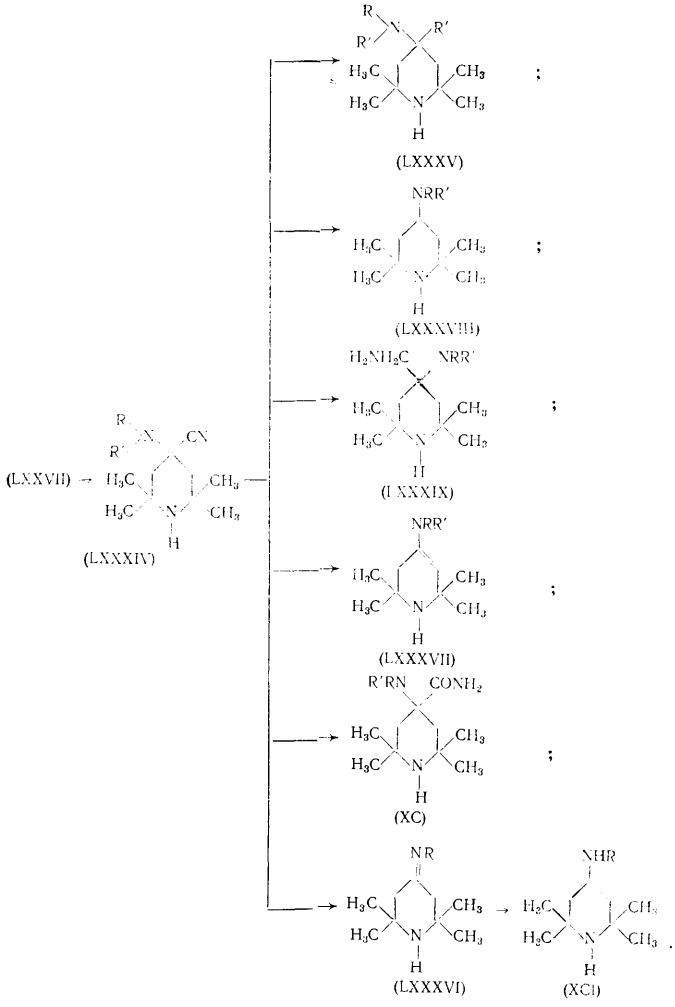
Using the appropriate Grignard reagents, 4-ethyl-(4-phenyl)-4-hydroxy-2,2,6,6-tetramethylpiperidines (LXXVI, R = C_2H_5 or C_6H_5) have been synthesised from triacetoneamine,[158] while the reaction with acetone cyanohydrin yielded 4-cyano-4-hydroxy-2,2,6,6-tetramethylpiperidine (LXXVII),[109] which was hydrolysed to 4-hydroxy-2,2,6,6-tetramethylpiperidine-4-carboxylic acid (LXXVIII)[109] and reduced to the diol (LXXIX).

Compound (I) has been converted by acetylene synthesis into 4-ethynyl-4-hydroxy-2,2,6,6-tetramethylpiperidine (LXXX), whose oxidation by oxygen in the presence of copper ammine gives rise to 1,4-bis(4-hydroxy-2,2,6,6-tetramethylpiperidin-4-yl)butadiene (LXXXI).[39] The triple bonds were reduced catalytically in the formation of compound (LXXXI).[39]

Compound (I) has been converted by reaction with sodium cyanide and ammonium carbonate into the piperidinohydantoin derivative (LXXXII),[115] which was then hydrolysed to the aminoacid (LXXXIII):



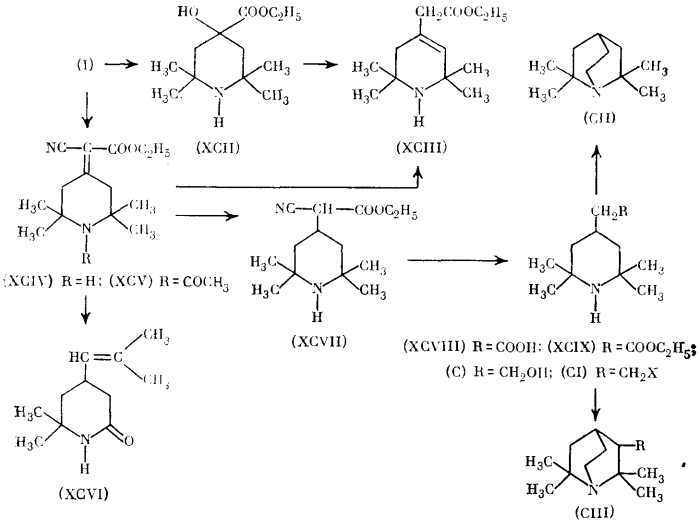
The reaction of the cyanohydrin (LXXVII) with ammonia or various aliphatic and aliphatic-aromatic amines in methanol readily gives rise to 4-amino-4-cyano-2,2,6,6-tetramethylpiperidines (LXXXIV) even at 0–20 °C.[110,111] Aromatic amines do not enter into this reaction.[110] The interaction of the aminonitriles (LXXXIV) with Grignard reagents leads to 4-alkyl-4-amino-2,2,6,6-tetramethylpiperidines (LXXXV),[111] while heating of compounds (LXXXIV) above 50 °C causes the splitting of hydrogen cyanide and the formation of the imino-derivatives (LXXXVI) or (in the case of tertiary amines) the enamines (LXXXVII).[110] On treatment with lithium tetrahydroaluminate, the aminonitriles (LXXXIV) readily lose their cyano-group and are converted into the *N'*-substituted 4-amino-2,2,6,6-tetramethylpiperidines (LXXXVIII) and only in the case where R = H and R' = H or $CH_2C_6H_5$ in compound (LXXXIV) are the triamines (LXXXIX) produced.[110] The hydrolysis of the nitrile group to the amide group in the aminonitriles (LXXXIV) is achieved with 90% sulphuric acid at 100 °C. Triacetoneamine is then formed together with the aminoamides (XC).[112] The imino-derivatives (LXXXVI) have been reduced catalytically to the corresponding amines (XCI).[159]



The condensation of triacetoneamine with ethyl bromoacetate under the conditions of the Reformatskii reaction results in the formation of 4-ethoxycarbonylmethyl-4-hydroxy-2,2,6,6-tetramethylpiperidine (XCII),[160] which can be dehydrated to the unsaturated ester (XCIII) by reaction with thionyl chloride or phosphoryl chloride. The corresponding methyl ester and the free acid have also been obtained from the product of the reaction of compound (I) with cyanoacetic ester.[160] The Knoevenagel condensation of compound (I) with cyanoacetic ester takes place readily in the presence of ammonium acetate in boiling benzene in the course of 1 h. More prolonged boiling in benzene or the use of higher-boiling solvents (toluene, xylene) lead to

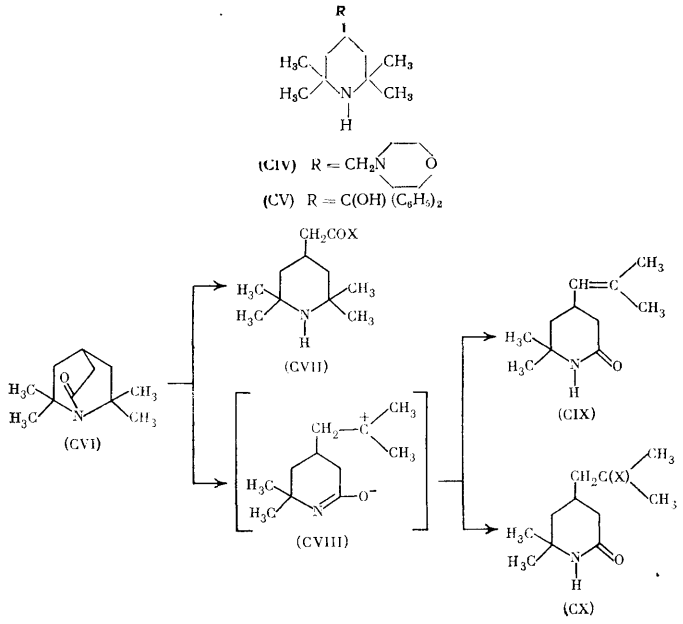
the *N*-acetylation of compound (XCIV) and the rearrangement of the resulting compound (XCV) to the unsaturated piperidinone (XCVI).[160] The hydrolysis of the nitriloester (XCIV) and subsequent partial decarboxylation are accompanied by the migration of the double bond to an endocyclic position and the ester (XCIII) is obtained after subsequent esterification.[161] Catalytic reduction of the exocyclic double bond in compound (XCIV) with the aid of palladium proceeds much more readily than the reduction of the endocyclic double bond in compound (XCIII). In order to synthesise the saturated acid (XCVIII), compound (XCIV) is therefore hydrogenated in a neutral medium in the presence of a palladium catalyst (in the presence of nickel or in hydrogenation using palladium and platinum in an acid medium, the nitrile group is involved) and the resulting compound (XCVII) is hydrolysed and partly decarboxylated. The high yield in the intermediate stages make it possible to carry out the process without isolating compounds (XCIV), (XCVII), and (XCVIII) and to obtain compound (XCIV) after esterification in an overall yield of 50% relative to triacetoneamine.[161]

The reduction of the ester (XCIX) with lithium tetrahydroaluminate, the subsequent substitution of the hydroxy-group by halogen, and cyclisation lead to 2,2,6,6-tetramethylquinuclidine (CII):[42,161]



Treatment of compound (XCVII) with alkyl halides in the presence of alkali metal alkoxides makes it possible to obtain derivatives *C*-alkylated in the side chain which have been converted into 3-alkyl-2,2,6,6-tetramethylquinuclidines (CIII) in accordance with schemes analogous to that described above.[44]

The conversion of the acid (XCVIII) into morpholide and the reduction of the latter with lithium tetrahydroaluminate led to the formation of 2,2,6,6-tetramethyl-4-(*N*-morpholinomethyl)piperidine (CIV)[46] and the reaction of the ester (XCIX) with phenyl-lithium afforded (2,2,6,6-tetramethylpiperidin-4-yl)diphenylmethanol (CV).[46]



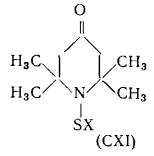
The conversion of the acid (XCVIII) into the chloride and treatment of the latter with triethylamine made it possible to synthesise 6,6,7,7-tetramethyl-2-quinuclidinone (CVI)[162,163]—a compound which is formally a bicyclic amide. However, its rigidly fixed structure with its unbound electron pair of the bridgehead nitrogen atom directed in space along the symmetry axis of the molecule rules out the possibility of the overlap of the above pair of *p* electrons with the π electrons of the C=O bond. As a result, compound (CVI) lacks the mesomeric effects characteristic of amides, the nitrogen atom exerts a purely inductive influence on the neighbouring carbonyl group, and compound (CVI) lacks amide properties but is a highly reactive acylating agent.[164,165] Its bridgehead nitrogen atom retains its highly nucleophilic properties in quaternisation and protonation reactions (pK_a = 6.37 ± 0.05 in water) and its carbonyl group has ketone and not amide properties [in the infrared spectra ν(CO) = 1755 cm^{-1} for the base, 1811 cm^{-1} for the hydrochloride, and 1820 cm^{-1} for the methiodide; it is reduced by lithium tetrahydroaluminate to CHOH and not to the CH_2 group, etc.]. Compound (CVI) reacts with various protic nucleophiles (water, alcohols, amines, etc.), the reaction involving the dissociation of the CO–N bond and the formation of 2,2,6,6-tetramethylpiperidine-4-acetic acid or its derivatives (esters, amides, etc.) (CVII). The reaction with nucleophiles in aprotic media (phenyllithium in ether, phosphorus pentachloride in benzene, excess of acetone cyanohydrin, lithium tetrahydroaluminate) entails the dissociation of the N–$C(CH_3)_2$ bond and the carbonium ion (CVIII) formed initially is stabilised either via deprotonation with formation of 4-(2-methyl-1-propenyl)-2-piperidinone (CIX) or via the addition of nucleophilic residues and the formation of substances of type (CX).

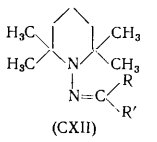
V. CHARACTERISTIC FEATURES OF THE CONFORMATIONS OF SHIELDED PIPERIDINE DERIVATIVES

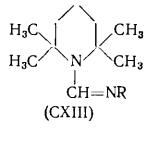
Data concerning the conformation of the 2,2,6,6-tetramethylpiperidin-1-yloxy-radical, a stable iminoxy-radical, have already been presented above. In recent years increasing attention has been devoted to the investigation of the characteristic features of the conformations of diamagnetic

sterically hindered 2,2,6,6-tetra-substituted piperidines. The preferential chair conformation of triacetoneamine and 1,2,2,6,6-pentamethyl-4-piperidinone has been established by ^{1}H NMR and the dipole moment and electro-optical Kerr effect methods, in the latter case with an equatorial orientation of the N–CH_3 group.[166–168] For the corresponding 2,2,6,6-tetramethyl-4-phenyl-4-piperidinol and 1,2,2,6,6,-pentamethyl-4-phenyl-4-piperidinol, there is an equilibrium between the chair and boat conformations with a 10% content of the latter, stabilised by an intramolecular hydrogen bond.[167,169] In the series of 1-*S*-substituted triacetoneamines (CXI, X = CCl_3, C_6H_5, t-C_4H_9, or CH_3), the activation energy for rotation about the N–S bond is significantly lower than in the corresponding 2,2,6,6-unsubstituted 4-piperidinones.[170]

The application of ^{1}H and ^{13}C NMR and X-ray diffraction showed that the conformational changes in compounds of the type of derivatives of 2,2,6,6-tetramethyl-1-piperidinyliminomethylene (CXII) [49,171–174] and 2,2,6,6-tetramethyl-1-piperidinylmethyleneimine (CXIII) [173] are hindered and that their preferred conformation is one where the planes of the N=C bond and of the piperidine ring are at right angles. On passing to 2,6-dimethylpiperidine derivatives, the planes of the N=C bond and the piperidine ring are coplanar for axial methyl groups and at right angles for equatorial methyl groups. *N*-Nitroso-2,2,6,6-tetramethylpiperidine has a coplanar arrangement of the planes of the piperidine ring and the N=O group.[49–51]


(CXI)


(CXII)


(CXIII)

Photoelectron spectroscopic studies have shown that the introduction of four methyl groups in the 2,2,6,6-positions in the piperidine ring lowers the ionisation potential of the free electron pair of the nitrogen by 0.66 eV,[52] and the contribution of each axial methyl group is ~0.26 eV and that of the equatorial methyl group is ~0.1 eV.

Thus the introduction of 2,2,6,6-substituents into the piperidine ring lowers the conformational mobility of the latter, facilitates its opening accompanied by various rearrangements, increases the stability of nitroxy-, nitrothiyl, and other free radicals, increases significantly the ganglion-blocking activity of the compounds, and almost completely abolishes their analgesic activity.

The above effects are associated mainly with the steric influence of the four $\alpha,\alpha,\alpha',\alpha'$-substituents and create a basis for the practical application of substances of this class.

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Ordzhonikidze All-Union Institute
of Chemistry and Pharmacology,
Moscow

Translated from *Uspekhi Khimii*, 53, 1325-1351 (1984) U.D.C. 547.26.118

Phosphorus-containing Polysulphides (Methods of Synthesis and Chemical Properties)

B.A.Khaskin

The methods of synthesis and chemical properties of compounds containing the $>\!P(=X)-(S)_n-$ (X = O or S, n = 2-4) fragment are examined. The unusual chemical behaviour of phosphorus-containing polysulphides in the reactions with nucleophiles and electrophiles is discussed.
The bibliography includes 170 references.

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I. INTRODUCTION

Despite the fact that phosphorus-containing polysulphides have been know for a long time, their chemical properties have begun to be studied in detail only in recent years. Nevertheless the presence of phosphorus-containing fragments introduces a definite specificity into the chemical behaviour of these compounds, which differ appreciably in their reactivity from aliphatic and aromatic polysulphides.[1] It must also be emphasised that phosphorus-containing polysulphides are the starting materials for the synthesis of a wide variety of organophosphorus compounds, including those which are difficult to obtain by other means.

This review is devoted to phosphorus-containing polysulphides—the "symmetrical" polysulphides (I), in the molecules of which the polysulphide bridge links two phosphorus-containing groups, and the "asymmetric" polysulphides (II), where there is only one such group. This review is a first attempt at a survey of the methods of synthesis and chemical properties of these compounds.

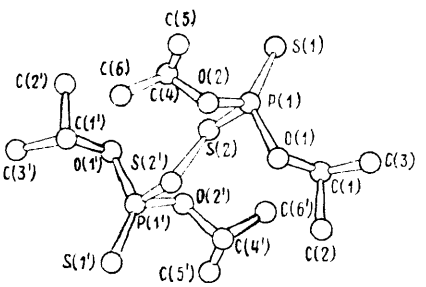
$$\underset{(I)}{R_2\overset{X}{\overset{\|}{P}}-S_n-\overset{X}{\overset{\|}{P}}R_2} \qquad \underset{(II)}{R_2\overset{X}{\overset{\|}{P}}-S_n-R'}$$

Here X = O or S, n = 2–4, and R and R′ are various organic and inorganic substituents linked to the phosphorus and sulphur atoms either directly or via the atoms of other elements.

Considerable advances have been made recently in the study of the reactivity of phosphorus-containing polysulphides and also in their employment for the synthesis of new structures among organophosphorus compounds.

II. THE STRUCTURE OF PHOSPHORUS-CONTAINING POLYSULPHIDES

The structure of symmetrical phosphorus-containing polysulphides is examined below in relation to bis(di-isopropoxythiophosphoryl) disulphide investigated by X-ray diffraction (see Figure).[2] The bond lengths and valence angles are indicated in Table 1. The data obtained do not preclude the possibility of the presence of a centre of symmetry located between the two sulphur atoms S(2) and S(2′). The S(2)–S(2′) distance (2.09 Å) is greater than in tetraethylthiuramide sulphide (1.999 Å).[3] The atoms surrounding the phosphorus atom have a distorted tetrahedral configuration; a plane can be drawn through the C(4)–O(2)–P(1)–O(1)–C(1) atoms to within 0.04 Å.



The structure of bis(di-isopropoxythiophosphoryl) disulphide according to Tkachev et al.[2]

Table 1. The bond lengths and valence angles in bis(di-isopropoxythiophosphoryl) disulphide.[2]

Bond length, Å		Valence angles, deg	
S(1)—P(1)	1.89	S(2′)—S(2)—P(1)	99.1
S(2)—P(1)	2.07	S(1)—P(1)—S(2)	102.8
S(2)—S(2′)	2.09	S(1)—P(1)—O(1)	122.0
P(1)—O(1)	1.57	S(1)—P(1)—O(2)	117.0
P(1)—O(2)	1.53	S(2)—P(1)—O(1)	108.0
O(1)—C(1)	1.44	S(2)—P(1)—O(2)	111.0
O(2)—C(4)	1.47	O(1)—P(1)—O(2)	95.0
C(1)—C(2)	1.52	P(1)—O(1)—C(1)	121.0
C(1)—C(3)	1.49	P(1)—O(2)—C(4)	119.0
C(4)—C(5)	1.55	O(1)—C(1)—C(2)	108.0
		O(1)—C(1)—C(3)	104.0
		O(2)—C(4)—C(5)	106.0
		O(2)—C(4)—C(6)	104.0
		C(3)—C(1)—C(2)	112.0
		C(5)—C(4)—C(6)	112.0

In the case of phosphorus-containing tri- and tetrasulphides, the structure of the polysulphide chain is of interest. Combined infrared and Raman spectroscopic data show

that the R–S–$(S)_n$–S–R polysulphide chain in phosphorus-containing polysulphides is unbranched.[4] Table 2 presents the absorption maxima in the infrared and Raman spectra of bis(diethoxythiophosphoryl) polysulphides in the range 400–700 cm^{-1} when the stretching vibration bands of the S–S, P–S, and P=S bonds are located. Evidently the bands which are intense in the Raman spectra have a low intensity in the infrared spectra and conversely. The unbranched nature of the structure of phosphorus-containing polysulphides is indicated by the fact that this feature holds best for centro-symmetric structures.[5] It must be emphasised that the bands cannot be assigned to different conformers, since the relative intensities remain constant as the temperature is altered.

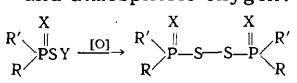
Table 2. The band maxima (ν, cm^{-1}) in the infrared and Raman spectra of bis(diethoxythiophosphoryl) polysulphides (bands of low intensity are indicated in brackets).[4]

P–S–S–P		P–S–S–S–P		P–S–S–S–S–P		Assignment
i.r.	R	i.r.	R	i.r.	R	
—	—	—	—	(452)	452	S–S sym.
—	—	464	465	469	—	S–S asym.
—	485	—	480	—	474	S–S sym.
498	—	501	—	501	—	P–S asym.
—	507	—	(506)	—	(505)	P–S sym.
639	(640)	643	(642)	644	—	P = S asym.
(656)	657	—	655	—	653	P = S sym.

III. METHODS OF SYNTHESIS

1. Symmetrical Phosphorus-containing Disulphides

The commonest method of synthesis of phosphorus-containing disulphides involves the oxidation of phosphorothioic and phosphorodithioic acids or their salts. The oxidants employed are the halogens (chlorine, bromine, and iodine),[6–19,21] hydrogen peroxide,[6,20,22] sodium nitrite (in the presence of sulphuric acid),[22–24] nitrous acid,[25] dimethylsulphoxide,[26] sulphuryl or thionyl chloride,[27–30] potassium hexacyanoferrate(III),[31] and atmospheric oxygen:[32]



where X = O or S, Y = H or a metal, and R and R′ are substituted or unsubstituted alkyl, aryl, alkoxy-, aryloxy-, or amino-group or a fluorine atom.

Best results are achieved when one employs acid salts, since the reactions of certain dialkylphosphorodithioic acids with iodine in an acid medium are reversible.[33] In an alkaline medium the oxidation by iodine proceeds as far as the phosphates and sulphates and it is therefore not possible to obtain disulphides under these conditions.[34,35]

It must be emphasised that, together with the disulphides, trisulphides are formed in yields up to 12% in the oxidation of phosphorodithioic acids by certain oxidants (Br_2, KI + I_2, H_2O_2) in an acid medium.[9,21] Concentrated sulphuric acid converts phosphorodithioic acids into a mixture containing up to 49% of the disulphide, 27% of the trisulphide, and 11% of phosphorothioic acid.[22] The ease of the oxidation of *O,O*-dialkyl phosphorodithioates depends on the nature of the alkyl residue (Table 3).

Phosphorus-containing disulphides with a C–P bond can be obtained from secondary phosphines via stages involving the formation of phosphinothious and phosphinodithioic acids with subsequent oxidation:[38]

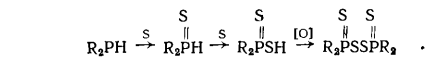
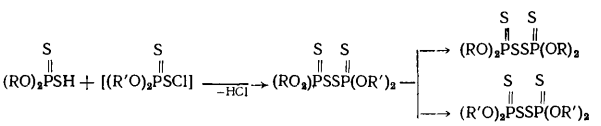


Table 3. The oxidation-reduction potentials *E* for the reaction $(RO)_2P(S)S^- - e \rightarrow (RO)_2P(S)SS(S)P(OR)_2$.[36,37]

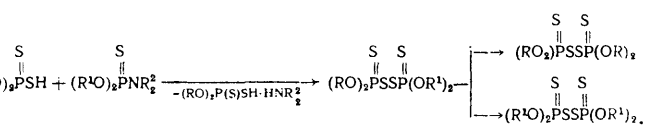
R	*E*, V	R	*E*, V
CH_3	0.315	C_6H_{13}	0.015
C_2H_5	0.255	iso-C_3H_7	0.196
C_3H_7	0.187	iso-C_4H_9	0.158
C_4H_9	0.122	iso-C_5H_{11}	0.086
C_5H_{11}	0.050		

Disulphides are formed from phosphorodithioic acids when the latter interact with dialkoxythiophosphorylsulphenyl chlorides:[39–42]

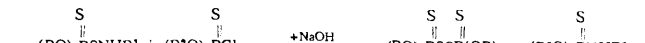


Symmetrical phosphorus-containing disulphides (R = R′) have been obtained successfully by this method. In the case of various alkyl groups (R and R′), the isolation of the disulphide in a pure form present considerable difficulties owing to the ease of their disproportionation to the corresponding symmetrical disulphides.[40]

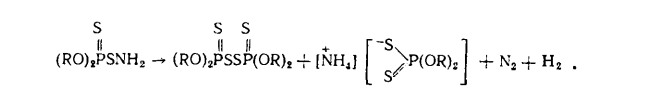
The reactions of phosphorodithioic acids with dialkoxythiophosphorylsulphenamides proceed analogously:[40]



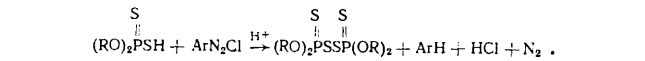
The interaction of *N*-substituted thiophosphorylsulphenamides with phosphorus acid halides in an alkaline medium results in the formation of phosphorus-containing disulphides:[43]



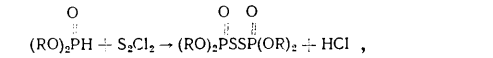
The decomposition of thiophosphorylsulphenamides, which apparently proceeds via a free-radical mechanism, also leads to the formation of disulphides:[44]



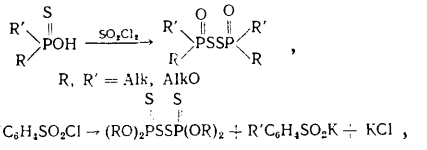
According to Mel'nikov and co-workers,[45,46] the formation of phosphorus-containing disulphides in the reactions of phosphorodithioic acids with diazonium salts in an acid medium also involves a free-radical mechanism:



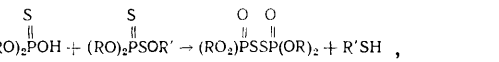
Several specific methods whereby one can obtain bis(dialkoxyphosphoryl) disulphides have been discussed in the literature. These include the reactions of dialkyl phosphites with sulphur monochloride,[47] i.e.



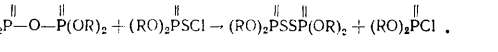
the condensation of acid phosphinothioates, phosphonothioates, phosphorothioates, and phosphorodithioates in the presence of sulphuryl chloride[29,30] or sulphonyl chlorides,[91] i.e.



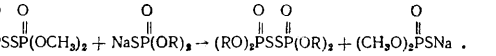
the reactions of *O,O*-dialkylphosphorodithioic acids with *O,O*-dialkyl *S*-methyl phosphorodithioates,[48] i.e.



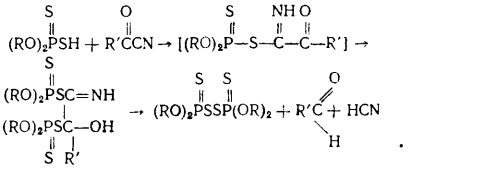
and the interaction of pyrophosphorothioates with dialkoxyphosphorylsulphen chlorides,[49]



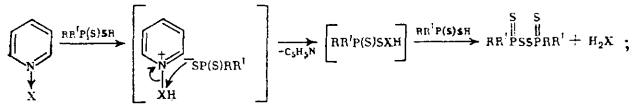
Bis(dialkoxyphosphoryl) disulphides with higher alkyl substituents (propyl and butyl) can be obtained from bis(dimethoxyphosphoryl) disulphide by its interaction with aqueous solutions of the salts of the corresponding phosphorus acids:[20]



Phosphorus-containing disulphides are obtained as side products in certain reactions. For example, the interaction of phosphorodithioic acids with nitriles of pyruvic and benzoylformic acids results in the formation of a bisphosphorylated iminocarbinol, one of the decomposition pathways of which leads to a phosphorus-containing disulphide:[50]



Disulphides are also formed in the reaction of phosphorodithioates with sulphimines, *N*-iminopyridinium betaines, and pyridine *N*-oxide:[51–53]

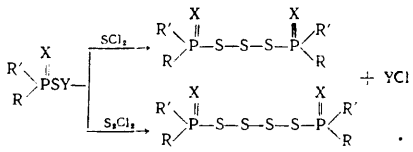


R, R' = C$_6$H$_5$, AlkO; X = O, NC$_6$H$_4$NO$_2$-4, NCOC$_6$H$_5$.

2. Symmetrical Phosphorus-containing Tri- and Tetrasulphides

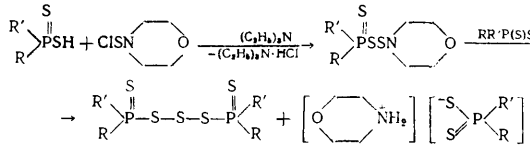
A phosphorus-containing trisulphide was isolated for the first time in the recrystallisation of diethyl phosphinodithioate from carbon disulphide and was described as bis(diethylphosphinyl) trisulphide.[54] A mixture of symmetrical tri- and tetra-sulphides is formed in the interaction of alcohols with phosphorus pentasulphides. Depending on the conditions (temperature, duration of heating), the content of trisulphides in the mixture can then range from 37 to 63% and that of the tetrasulphides from 19 to 28%.[37,55]

The commonest method of synthesis of phosphorus-containing tri- and tetra-sulphides involves the interaction of phosphorodithioic acids or their salts with sulphur di- or mono-chloride:[6,7,56–60]

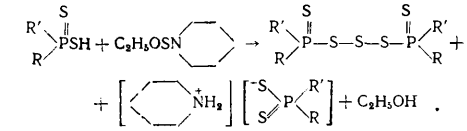


where Y = H or metal, X = O or S, and R,R' is an alkyl-, alkoxy-, or substituted alkoxy-group[6,7,56,58] or R = alkyl and R' = S.[59,60]

Symmetrical phosphorus-containing trisulphides have been obtained from *O,O*-dialkylphosphorodithioic or alkoxyalkylphosphonodithioic acids and morpholinylsulphenyl chloride.[41–61] The reaction apparently proceeds via the intermediate formation of thiophosphoryl morpholino disulphide:

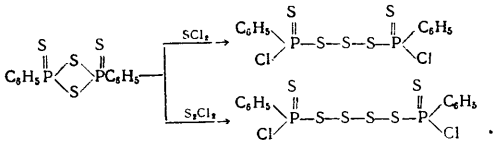


The reaction with ethoxypiperidino sulphide proceeds analogously:[42]

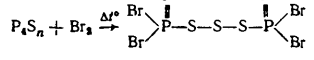


When dialkoxythiophosphoryl *N*-mono(di)alkylamino disulphides were allowed to interact with phosphorothioic acids, bis(dialkoxythiophosphoryl) tetrasulphides were isolated.[62]

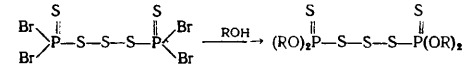
Halogen-substituted phosphorus-containing polysulphides are extremely interesting. Fluorine-substituted polysulphides are obtained by oxidising the corresponding fluorine-containing phosphorodithioic acids.[59,60] Bis(phenylchlorothiophosphonyl) polysulphides are obtained by treating phenylthionophosphine sulphide with sulphur di- or monochloride:[63]



Bis(dibromothiophosphoryl) trisulphides are formed readily when phosphorus polysulphides P_4S_n, where n = 3, 5, or 7, are treated with bromine:[64,65]



The interaction of bis(dibromothiophosphoryl) trisulphides with alcohols gives rise to bis(dialkoxythiophosphoryl) trisulphides:[65]



Individual reactions leading to the formation of phosphorus-containing tri- and tetra-sulphides as side products are known in the literature. Thus bis(diethylthiophosphinyl) trisulphide can be isolated in a low yield in the reaction of bis(dimethylamino)diethylphosphinylborane with sulphur:[66]

$$[(CH_3)_2N]_2BP(C_2H_5)_2 + S \rightarrow (C_2H_5)_2\overset{S}{\overset{\|}{P}}-S-S-\overset{S}{\overset{\|}{P}}(C_2H_5)_2 + B_2[N(CH_3)_2]_4 \quad .$$

Phosphorus-containing polysulphides are formed together with phosphinodithioic acids and disulphides in the interaction of secondary phosphines with sulphur.[54]

In the oxidation of potassium and nickel salts of *O,O*-diethylphosphorodithioic acids with selenous acid, bis(diethoxythiophosphoryl) tetrasulphide is one of the reaction products.[67]

3. Asymmetric Phosphorus-Containing Polysulphides

Phosphorothioic and phosphorodithioic acids or their salts can be used to synthesise asymmetric phosphorus-containing disulphides. On interaction with various organosulphenyl chlorides, they give rise to a wide variety of disulphides:[42,68-81]

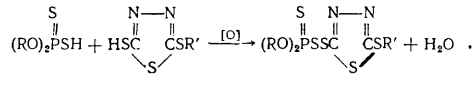
$$(RO)_2\overset{X}{\overset{\|}{P}}SY + ClSR' \rightarrow (RO)_2\overset{X}{\overset{\|}{P}}SSR' + YCl \ ,$$

where X = O or S, Y = H or metal, and R′ = alkyl, substituted alkyl, aryl, substituted aryl, carbamoyl, alkoxycarbonyl, and various ester and heterocyclic groups.

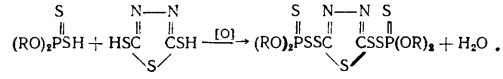
Phosphorodithioic acids react with aminosulphenyl chlorides to form dialkoxythiophosphoryl amino disulphides:[41,61,68-70]

$$(RO)_2\overset{S}{\overset{\|}{P}}SY + ClSNR_2' \rightarrow (RO_2)\overset{S}{\overset{\|}{P}}SSNR_2' + YCl \ .$$

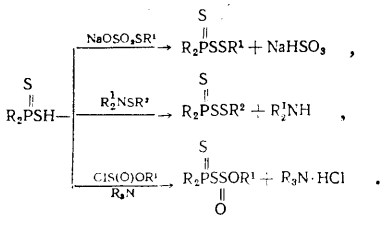
Asymmetric phosphorus-containing disulphides with thiadiazole residues are obtained by the joint oxidation of *O,O*-dialkylphosphorodithioic acids and 2-mercapto-1,3,4-thiadiazoles:[82]



In the presence of a twofold excess of phosphorodithioic acid, compounds with two symmetrical disulphide groups are formed analogously from dimercapto-derivatives:



Asymmetric phosphorus-containing disulphides and sulphonylthio-derivatives can also be obtained by the reaction of phosphorodithioic acids with sodium alkyl thiosulphates,[83] sulphenamides,[61,85] and alkylsulphurous acid chlorides:[84]

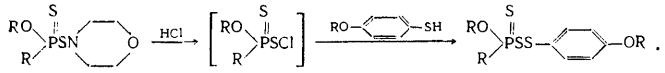


Many asymmetric phosphorus-containing disulphides are obtained by the reaction of dialkoxyphosphoryl- and dialkoxythiophosphoryl-sulphenyl chlorides with compounds containing the mercapto-group:[76,86-88,93]

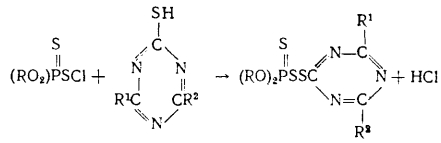
$$(RO)_2\overset{X}{\overset{\|}{P}}SCl + R'SH \rightarrow (RO)_2\overset{X}{\overset{\|}{P}}SSR' + HCl \ .$$

It is noteworthy that, in contrast to phosphorylsulphenyl chlorides, the majority of thiophosphorylsulphenyl chlorides are unstable. However, in many studies these substances were isolated in a pure form using various organophosphorus compounds as intermediates in the synthesis.[39,61,89]

The preparation of asymmetric disulphides from thiophosphorylsulphenamides in the presence of HCl should be assigned to reactions of the same type, since the corresponding thiophosphorylsulphenyl chloride is an intermediate under these conditions:[61]



The interaction of dialkoxythiophosphorylsulphene chlorides with mercaptotriazines in the presence of an acceptor which absorbs the hydrogen chloride evolved leads to dialkoxythiophosphoryl triazinyl disulphides:[90]

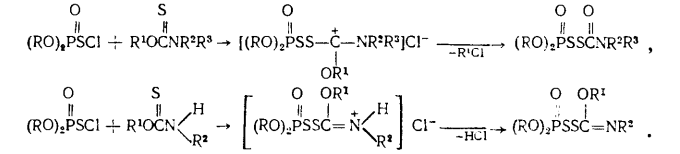


Dialkoxythiophosphorylsulphene chlorides react with derivatives of carbonic and carbamic acids to give the corresponding phosphorus-containing disulphides:[92]

$$(RO)_2\overset{O}{\overset{\|}{P}}SCl + R^1S\overset{X}{\overset{\|}{C}}R^2 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}S\overset{X}{\overset{\|}{C}}R^2 + R^1Cl \ ,$$

where X = O or S, R = alkyl, R^1 = H, a metal, or alkyl, and R^2 = alkoxy-, aryloxy-, or amino-group.

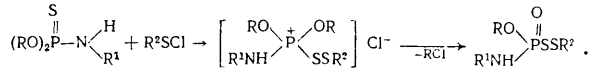
Certain alkoxythiocarbamates also react with dialkoxyphosphorylsulphenyl chlorides. It is remarkable that, depending on the structure of the substituent at the nitrogen atom, final reaction products of different structure are formed:[92]



It has been noted in some reports that, on heating or prolonged storage, compounds containing the thiocarbamoyl residue are converted from the thiolo- into the thiono-form:[92]

$$(RO)_2\overset{O}{\overset{\|}{P}}S\overset{S}{\overset{\|}{C}}NR^1R^2 \rightarrow (RO)_2\overset{S}{\overset{\|}{P}}O\overset{S}{\overset{\|}{C}}NR^1R^2 \ .$$

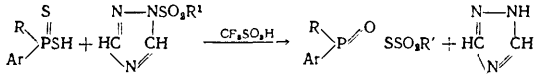
Asymmetric phosphorus-containing disulphides are also the products of the reactions of phosphorothioic acid amides with organosulphenyl chlorides. The formation of a disulphide in this instance is apparently a consequence of the decomposition of the intermediate quasi-phosphonium compound:[94]



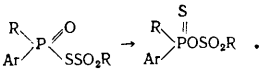
A novel method of synthesis of diethoxyphosphoryl acetyl disulphide from *O,O*-diethyl *S*-methyl phosphorodithioate and thioloacetic acid has been proposed by Michalski and coworkers:[48]

$$(RO)_2\overset{O}{\overset{\|}{P}}SOCH_3 + CH_3CSH \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}SS\overset{O}{\overset{\|}{C}}CH_3 + CH_3OH \ .$$

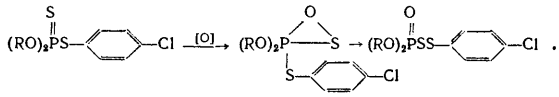
The method of synthesis of sulphonylthio-derivatives by sulphonating sulphotriazoles with alkylarylphosphinodithioic acids in the presence of trifluoromethanesulphonic acid[84] is also of interest:



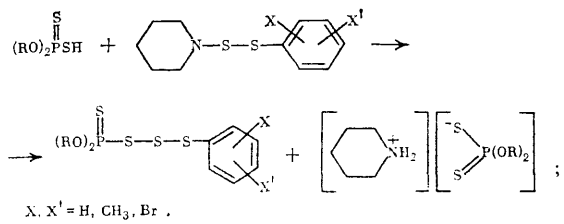
Analogously to compounds containing the thiocarbamoyl residue,[92] *S*-sulphonylphosphinothioates slowly isomerise to the corresponding P–S derivatives at 20 °C:[84]



Asymmetric phosphorus-containing disulphides are obtained by oxidising the esters of phosphorodithioic acid with 3-chloroperbenzoic acid. Three-membered heterocycles are apparently formed as intermediates in this reaction:[95]

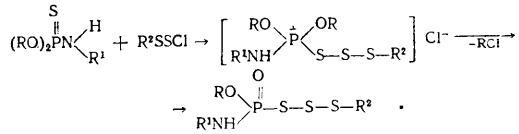


Asymmetric phosphorus-containing trisulphides have been investigated to a much smaller extent. Several examples of the preparation of such compounds have been described in the literature. One of these involves the interaction of *O*,*O*-dialkylphosphorodithioic acids with amino disulphides:[96]



X, X' = H, CH_3, Br .

Trisulphides are also formed in the reactions of phosphorothioic acid amides with organothiosulphene chlorides:[97]



IV. CHEMICAL PROPERTIES

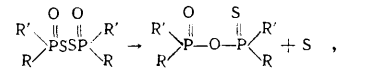
Despite the fact that phosphorus-containing polysulphides are quite readily available, systematic studies of their reactions have been begun comparatively recently and have led to the development of methods of synthesis of a number of classes of organophosphorus compounds whose preparation by other methods presents significant difficulties.[1,97]

The presence of several reaction centres in the molecules of phosphorus-containing polysulphides imparts unusual features to their chemical behaviour. These compounds react with both electrophiles and nucleophiles, the reactions involving and not involving the rupture of the polysulphide chain.

Among the phosphorus-containing polysulphides, the disulphides are the most thoroughly investigated group; tri- and tetra-sulphides have been studied to a much lesser extent.

1. Thermal Stability

The thermal stability of phosphorus-containing polysulphides depends to a large extent on their structure. Thus, whereas bis(diethoxythiophosphoryl) disulphide begins to decompose only at 180 °C,[98] the corresponding dialkyl-, dialkoxy-, and alkylalkoxy-phosphoryl compounds are gradually converted into pyrophosphorothioates, even at room temperature, while on heating the process is rapid:[29]



where R and R' = alkyl or alkoxy-group.

Analogous behaviour has also been observed in the series of tri- and tetra-sulphides. Bis(dialkoxythiophosphoryl) trisulphides and bis(dialkoxythiophosphoryl) tetrasulphides are comparatively stable at room temperature, but on heating or prolonged storage they decompose with liberation of sulphur.[4] Bis(dialkoxyphosphoryl) trisulphides and bis(dialkoxyphosphoryl) tetrasulphides are much less stable; they begin to evolve sulphur at room temperature after only several days.[4]

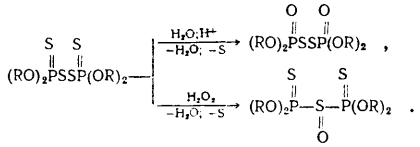
2. Oxidation and Chlorination

Bis(dialkoxythiophosphoryl) disulphides are quantitatively oxidised by iodine in an aqueous alkaline medium:[34,35]

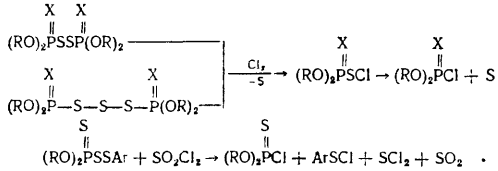


An analogous reaction takes place also when other oxidants are employed.[7]

Depending on the reaction conditions, the oxidation of bis(dialkoxythiophosphoryl) disulphides with hydrogen peroxide can give rise to both bis(dialkoxyphosphoryl) disulphides[99] and bis(dialkoxythiophosphoryl) sulphoxides:[100]



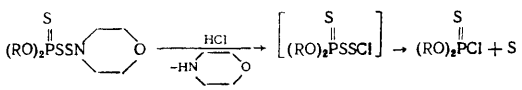
The chlorination of various symmetrical and asymmetric phosphorus-containing disulphides and trisulphides with chlorine or sulphuryl chloride entails the rupture of the polysulphide chain with formation of phosphoryl- or thiophosphoryl- sulphenyl chlorides,[6,9,101–104] but, under the reaction conditions, the latter evolve sulphur, giving rise to phosphorothioic acid chlorides as the final products:



The chlorination or bromination of bis(hexafluorodimethylthiophosphinyl) disulphide leads to the chloride or bromide of hexafluorodimethylphosphinous acid;[105] this disulphide reacts with hydrogen chloride or bromide to form mixtures of hexafluorodimethylphosphinodithioic acid and its halide.[105]

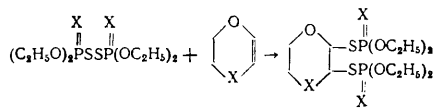
The reaction of dialkoxythiophosphoryl morpholino disulphide with hydrogen chloride proceeds with rupture of the S–N bond. According to Almasi and Plaskucz,[41] the unstable

dialkoxyphosphoryl chloride sulphide is an intermediate in this reaction:



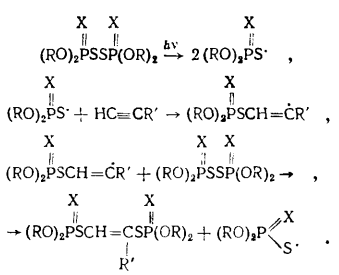
3. Addition to Multiple Bonds

An interesting type of reaction of phosphorus-containing disulphides is addition to multiple bonds.[106,107] Bis(diethoxyphosphoryl) bis(diethoxythiophosphoryl) disulphides react with dioxene and thioxene in the presence of iodine to form the corresponding phosphorothioic acid esters:



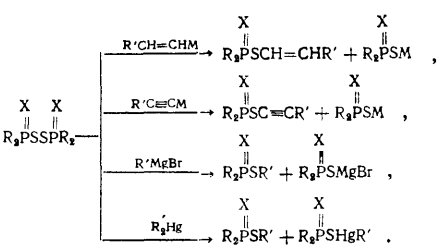
where X = O or S.

The reaction of phosphorus-containing disulphides with acetylenic hydrocarbons takes place under irradiation with ultraviolet light and apparently has a radical mechanism:[108]



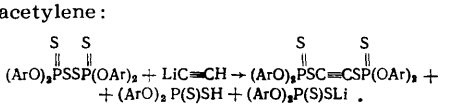
4. Interaction with Organometallic Compounds

Phosphorus-containing disulphides react with organometallic compounds with dissociation of the disulphide bond and the formation of the corresponding phosphorothioic and phosphorodithioic acid esters.[109–113] The literature contains examples of such interaction with alkyl-lithium, alkylpotassium, alkylsodium, metal derivatives of alkenes and alkynes, Grignard reagents,[110–113] and organomercury compounds:[114]

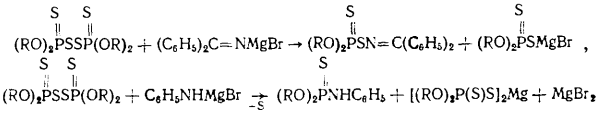


where R = aryl or alkoxy-group, X = O or S, and M is a metal.

Bis-derivatives are also sometimes formed, for example, from lithioacetylene:

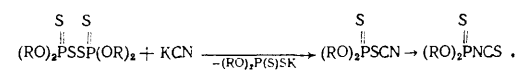


The reactions with *N*-magnesio-derivatives either give a low yield of the corresponding sulphenamides or phosphorothioic acid amides are formed as a result of desulphurisation:[113,115]

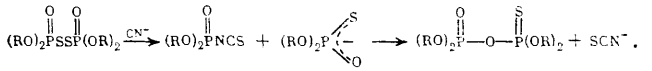


5. Reactions with Hydrocyanic Acid Salts

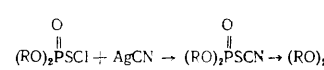
The reactions of hydrocyanic acid salts with bis(thiophosphoryl) disulphides involve the initial formation of the corresponding thiocyanates,[116,117] which subsequently isomerises to the isothiocyanates:



In the case of bis(phosphoryl) disulphides the final products of this reaction are either pyrophosphoromonothioates or, depending on the structure of the groups attached to the phosphorus atom, isothiocyanates:[49,118]



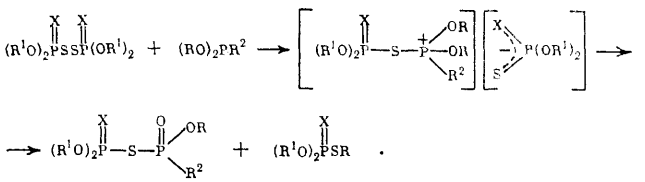
The thiocyanates of *O,O*-dialkylphosphoric acids, obtained by the reaction of phosphorylsulphenyl chlorides with silver cyanide, are stable only in solution at −5 °C. They isomerise at room temperature to the isothiocyanates:[49]



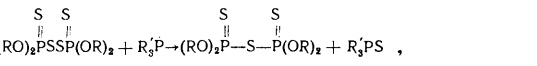
6. Reactions with Tervalent Phosphorus Derivatives

The interactions of bis(phosphoryl) and bis(thiophosphoryl) disulphides with various tervalent phosphoryl derivatives have been studied in detail.[49,119–128] Some of these reactions constitute convenient methods for the synthesis of many organophosphorus derivatives. It is most likely that such reactions proceed via the mechanism of the Arbuzov reaction with formation of an intermediate quasi-phosphonium salt.

The character of the final reaction product depends on the mode of decomposition of this intermediate. Thus bis(dialkoxyphosphoryl) and bis(dialkoxythiophosphoryl) disulphides react with phosphite and phosphonite esters to form pyrophosphates and the esters of phosphorothioic and phosphorodithioic acids,[49,119–123]

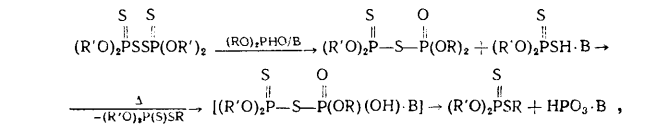


The reactions of phosphorus-containing disulphides with triaryl phosphites, phosphorous acids tris(*N,N*-diethylamide), and triphenylphosphine[123–125] proceed with the desulphurisation of the disulphides and the formation of pyrophosphorotrithioates:



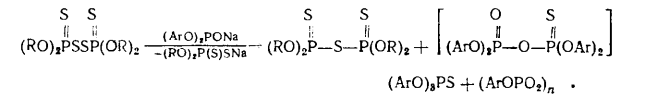
where R = alkyl or phenyl and R′ = phenyl, alkoxy-group, or diethylamino-group.

Bis(dialkoxythiophosphoryl) and bis(diaryloxythiophosphoryl) disulphides react with salts of phosphorous acid in accordance with the mechanism of the Michaelis–Becker reaction:[127,128]



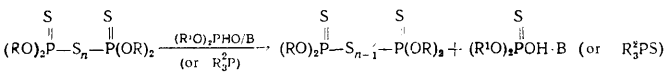
where B is a base.

The formation of pyrophosphorotrithioates and triaryl phosphorothioates has been observed in the reactions of bis(dialkoxythiophosphoryl) disulphides with alkali metal salts of diarylphosphorothioic acids:[124,128]



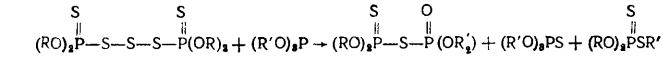
The formation of the triaryl phosphorothioate has been explained by the disproportionation of the tetra-aryl pyrophosphorothioate.

The interaction of phosphorus-containing tri- and tetrasulphides with an equimolar amount of dialkyl or trialkyl phosphite and also triphenylphosphine entails the desulphurisation of these compounds with formation of di- and tri- sulphides respectively:[142]

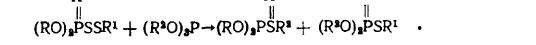


where R and R^1 is an alkyl, R^2 is an alkoxy-group or phenyl, n = 3 or 4, and B is a base.

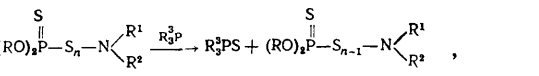
The reactions of phosphorus-containing tri- and tetrasulphides with tervalent phosphorus derivatives apparently proceed analogously to the reactions of the disulphides, via a stage involving the formation of an unstable quasi-phosphonium compound. However, in contrast to the disulphides, the intermediate formed is more polar and its desulphurisation is observed as a consequence of the rupture of the disulphide bond. In the presence of an excess of the di- or tri-aryl sulphite, the reaction does not stop at the stage described above: the disulphides formed react further with the phosphites to form asymmetric pyrophosphorodithioates as well as esters of phosphorothioic and phosphorodithioic acids:[129]



Asymmetric phosphorus-containing disulphides react with triethyl phosphites with rupture of the S–S bond to form the triesters of phosphorothioic and phosphorodithioic acids:[121,126]



In the reaction with trialkyl phosphites or triphenylphosphines, phosphorus-containing amino polysulphides undergo desulphurisation with formation of products containing one sulphur atom less:[62]

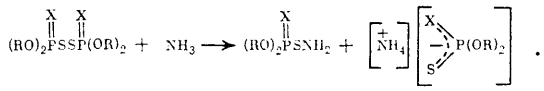


where n = 3 or 4 and R^3 is an alkoxy-group or phenyl.

7. Reactions with Ammonia, Amines, and Hydrazines

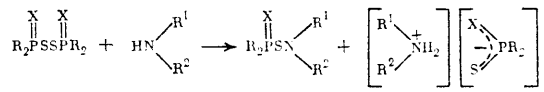
In the reactions of symmetrical phosphorus-containing disulphides with nitrogen-containing bases having a mobile hydrogen atom, the sulphide bond is broken and the corresponding phosphorylsulphenamides and the ammonium salts of phosphorothioic or phosphorodithioic acids are formed. The reaction is general for different amines.[44,130–135] With its aid, thiophosphorylsulphenamides unsubstituted at the nitrogen atom and *N*-monoalkyl-substituted derivatives have become available, whereas it had been impossible to obtain them by the methods known previously.[136]

On reaction with ammonia at approximately 5 °C, bis(dialkoxyphosphoryl) and bis(dialkoxythiophosphoryl) disulphides form high yields of dialkoxyphosphoryl- and dialkoxythiophosphoryl-sulphenamides:[44,137]



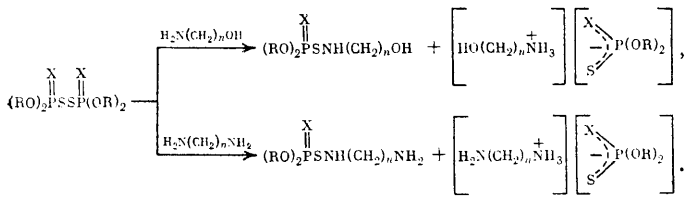
The reaction is rapid and the phosphorylsulphenamides obtained are vacuum-distilled. They are insufficiently stable on storage but are stable at low temperatures and can be used as intermediates in the synthesis of various derivatives.[138]

The substitution of a hydrogen atom in the amide group increases the stability of phosphorylsulphenamides. Thus primary and secondary aliphatic amines react with bis(phosphoryl) and bis(thiophosphoryl) disulphides to form more stable sulphenamides:[130,132,139,140]

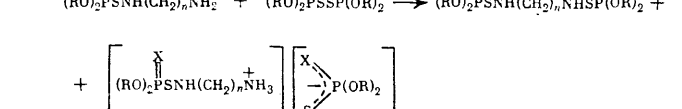


where R is an alkoxy- or aryloxy-group or aryl and X = O or S.

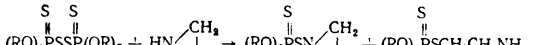
Hydroxyalkylamines and diamines react analogously:[134,141]



Aliphatic diamines can give rise to bisphosphorylated derivatives:[141]

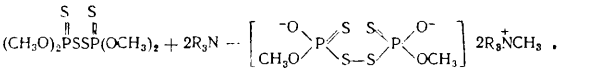


Alicyclic secondary amines react with disulphides in accordance with an analogous mechanism,[140,142] but the reaction with ethyleneimine involves the simultaneous opening of the three-membered ring together with the formation of thiophosphorylethyleneimide:[134]

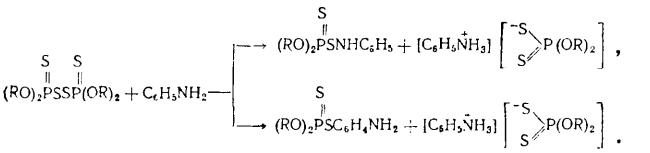


On reaction with tertiary amines, bis(dialkoxythiophosphoryl) disulphides behave as alkylating agents,[143,144] forming the salts of quaternary ammonium bases. This

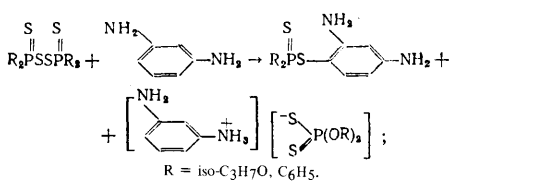
reaction takes place particularly readily with bis(dimethoxythiophosphoryl) disulphide:[143]



Bis(dialkoxythiophosphoryl) disulphides react with aromatic amines in an unusual manner.[145] The reaction with aniline at 90–95 °C takes place with rupture of the sulphide bond via two pathways with formation of *N*-phenylthiophosphorylsulphenamide and the product of the substitution of hydrogen in the aromatic ring by the thiophosphorylmercapto-group:

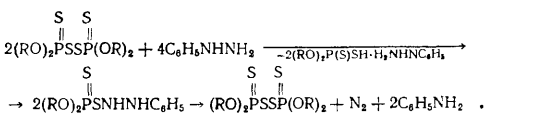


The reaction of phosphorus-containing disulphides with *m*-phenylenediamine proceeds under milder conditions (on heating a mixture of the initial components in benzene) and the main products are *S*-(diaminophenyl)-substituted derivatives of phosphorodithioic acids and substitution takes place in the 4-position of *m*-phenylenediamine:[145]



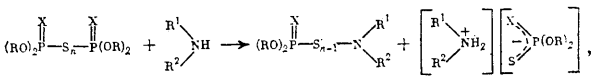
R = iso-C_3H_7O, C_6H_5.

The interaction of phosphorus-containing disulphides with aromatic and aliphatic hydrazines is also interesting. It is not possible to isolate the corresponding thiophosphorylsulphenichydrazide, which apparently decomposes with formation of the initial disulphide, aniline, and nitrogen. In the presence of an excess of phenylhydrazine, the disulphides react almost completely:[131]



In contrast to the reaction with phenylhydrazine, the analogous reaction of disulphides with *N*,*N*-dimethylhydrazine leads to the formation of the dimethylammonium salt of *O*,*O*-dialkylphosphorodithioic acid and not its dimethylhydrazinium salt.[131] This can be explained by the more basic properties of the dimethylamine formed compared with those of the initial dimethylhydrazine.

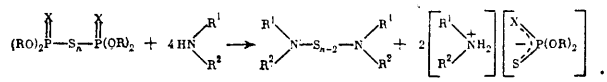
The reactions of phosphorus-containing tri- and tetrasulphides with amines had been virtually uninvestigated previously. Several studies devoted to the interaction of amines with the tri- and tetra-sulphides showed that the main product is the salt of the amine and the corresponding phosphorothioic acid; other phosphorus-containing reaction products could not be isolated.[57,65] It has been established in recent years that, in the interaction of phosphorus-containing tri- and tetra-sulphides with primary and secondary aliphatic or alicyclic amines, the disulphide bond nearest the phosphorus atom is ruptured with formation of the corresponding asymmetric polysulphides containing one sulphur atom less and of the salts of *O*,*O*-dialkylphosphorothioic or *O*,*O*-dialkylphosphorodithioic acids:[147,148]



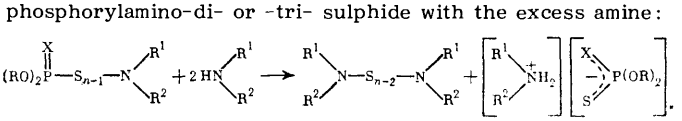
where X = O or S, *n* = 3 or 4, R = alkyl, R^1 = H or alkyl, and R^2 = alkyl (R^1 and R^2 can together form a heterocyclic group).

Dialkoxyphosphoryl *N*-mono(or *N*,*N*-di)alkylamino disulphides are readily vacuum-distilled, while the corresponding dialkoxyphosphoryl and dialkoxythiophosphoryl trisulphides decompose on distillation. The infrared, ^{1}H NMR, and ultraviolet spectra are most informative as regards these compounds. The infrared spectra contain the characteristic absorption band of the N–H group (3320 cm^{-1}), δ_{N-H} = 3.85–4.71 p.p.m. in the ^{1}H NMR spectra, while the ultraviolet spectra exhibit absorption at 226 and 281 nm for the di- and tri-sulphides respectively.[4] The stability of such structures is apparently due to the stabilisation of the molecule by the resonance interaction involving the 3*d* orbitals of the sulphur and phosphorus atoms, which is confirmed by the bathochromic shift of the absorption maximum in the ultraviolet spectra on passing from the disulphide to the trisulphide.[146,149]

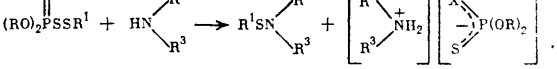
The reactions of tri- and tetra-sulphides with an excess of aliphatic amines result in a quantitative formation of bis(dialkylamino) sulphides or bis(dialkylamino) disulphides together with salts of phosphorothioic or phosphorodithioic acids:



This is explained by the reaction of the intermediate thiophosphorylamino-di- or -tri- sulphide with the excess amine:

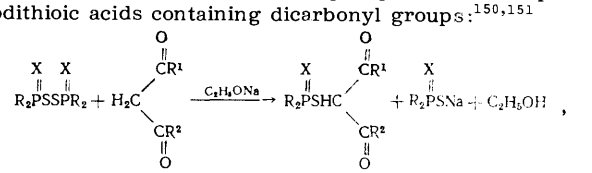


It must be emphasised that, in contrast to the reaction of symmetrical disulphides, the interaction of asymmetric phosphorus-containing disulphides with primary and secondary amines results in the formation of sulphenamides without a phosphorus atom, while the organophosphorus part of the molecule enters into the composition of the corresponding ammonium salt in the form of a phosphorus-containing anion:[94]



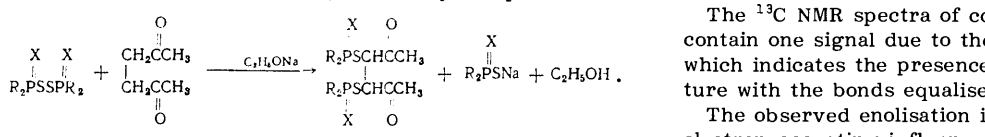
8. Reactions of Phosphorus-containing Polysulphides with a CH Acid

One of the characteristic pathways in the reactions of phosphorus-containing polysulphides involves their interaction with dicarbonyl compounds. Thus the reactions of phosphorus-containing disulphides with β- and γ-dicarbonyl compounds, namely with the sodio-derivatives of acetoacetic ester, acetylacetone, acetoacetanilide, malonic acid ester, and acetonylacetone involve the dissociation of the disulphide bond and the formation of esters of phosphorothioic or phosphorodithioic acids containing dicarbonyl groups:[150,151]



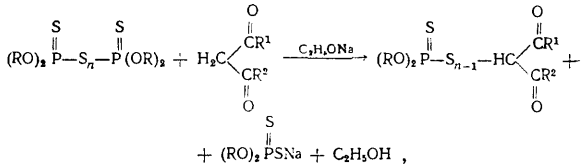
where R = aryl or alkoxy-group, $R^1 = CH_3$ or C_2H_5O, $R^2 = CH_3$, C_2H_5O, or C_2H_5NH, and X = O or S. It must be emphasised that the reaction leads to the formation of the corresponding *C*-derivative.[151]

Depending on the conditions (the ratio of the reactants and process temperature), the sodio-derivatives of γ-dicarbonyl compounds interact with either one disulphide molecule, as in the case of β-dicarbonyl derivatives, or with two such molecules to form disubstituted γ-dicarbonyl compounds:



The more mobile the hydrogen in the molecule of the carbonyl compound, the greater the ease of the reaction with phosphoryl disulphides.

In the interaction of phosphorus-containing tri- and tetrasulphides with the sodio-derivatives of malonic ester, acetoacetic ester, or acetylacetone, the disulphide bond nearest to the phosphorus atom is ruptured and the corresponding asymmetric di- or tri-sulphides are formed together with salts of phosphorodithioic acids:[152]

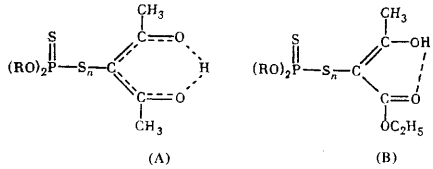


where R = alkyl, R^1 and R^2 = alkoxy-group or CH_3, and $n = 3$ or 4.

Table 4. Spectroscopic characteristics of diacetylmethyl and alkoxycarbonylacetylmethyl dialkoxythiophosphoryl polysulphides.[152]

n	^{1}H NMR spectrum (δ, p.p.m.)		I.r. spectrum (ν, cm^{-1})		^{13}C NMR spectrum (δ, p.p.m.)		U.v. spectrum	
	OH	CH_3	H . . . O	—C=C—	=C—CH_3	=C—OC_2H_5	λ_{max}, nm	lg ε
				Compounds of type (A)				
2	17.1	2.43	1570	—	195.77	—	231	3.1
3	17.6	2.45	1575	—	195.66	—	240	3.9
				Compounds of type (B)				
2	13.7	2.43	1580	1635	184.81	171.59	232	4.1
3	13.7	2.43	1585	1640	184.81	171.68	240	4.6

Analysis of the infrared, ultraviolet, and ^{1}H and ^{13}C NMR spectra showed that the di- and tri-sulphides formed, (A) and (B), are almost wholly enolised in both non-polar solvents and in a pure form. The chemical shift of the signal due to the hydroxyl proton in the ^{1}H NMR spectra (Table 4) indicates the formation of an intramolecular hydrogen bond between the enolic hydroxyl and the oxygen of the carbonyl group:



(A) (B)

Table 4 shows that the chemical shift of the signal of the enolic proton hardly changes with increase of temperature to 70 °C and following a change in the nature of the solvent, which indicates the stability of the chelate structure formed. The number of sulphur atoms in the chain also does not affect the chemical shift. The content of the enolic form in compounds of this type is 98%; on passing from CCl_4 as the solvent to CH_3CN, the content of the keto-form increases to 4%.[152]

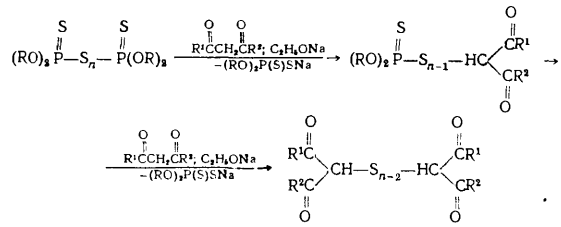
The ^{13}C NMR spectra of compounds of type (A) (Table 4) contain one signal due to the carbon of the carbonyl group, which indicates the presence of a quasi-symmetrical structure with the bonds equalised in pairs.[153]

The observed enolisation is a consequence of the strong electron-accepting influence of the thiophosphoryl disulphide and trisulphide groups, which entails a decrease of the electron density on the methyl carbon atom and hence an increase of the acidity of the CH group.

An increase of the wavelength and of the extinction coefficients in the ultraviolet spectra of compounds of types (A) and (B) (Table 4) on passing from the disulphide to the trisulphide indicates the presence in this compound of an unbranched structure of the polysulphide chain.[154]

The products of the reaction of phosphorus-containing polysulphides with sodiomalonic ester exist in the keto-form, as shown by the absorption band at 1740 cm^{-1} in the infrared spectra, the presence of the signal due to the proton in the CH group (δ = 4.4 p.p.m.), and the absence of the signal of the enolic proton in the ^{1}H NMR spectra.

In the interaction of symmetrical tri- or tetra-sulphides with an excess of a β-dicarbonyl compound, the disulphide bonds closest to the phosphorus atom are ruptured in succession and the corresponding mono- or di-sulphides without phosphorus are formed:[152]

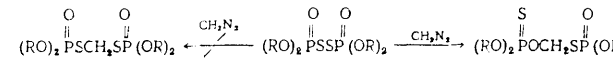


9. The Interaction of Phosphorus-containing Polysulphides with Diazo-compounds

The interaction of phosphorus-containing polysulphides with diazo-compounds has been studied only in recent years.[155-163] It is stated in the literature that aromatic disulphides, in particular diphenyl disulphide, react with the Simmons–Smith reagent (iodomethylzinc iodide ICH_2ZnI) and also with the esters of diazocarboxylic acids in the presence of a catalyst to form the products of the insertion of the corresponding carbene in the disulphide bond. On the other hand, dialkyl sulphides do not react with the Simmons–Smith reagent and the reaction with diazocarboxylic acid esters takes place with only an insignificant yield.[164,165]

These data show that the activity of the disulphides in relation to diazo-compounds is significantly influenced by their structure. The presence of electron-donating substituents reduces and that of electron-accepting substituents increases the reactivity of the disulphides. The latter factor is manifested in the reaction of phosphorus-containing polysulphides with diazo-compounds in reactions of the carbene and non-carbene types.

It is of interest that, in contrast to aromatic disulphides, bis(dialkoxyphosphoryl) disulphides never form products of the insertion of the methylene group in the S–S bond on reaction with an excess of diazomethane in an ethereal solution under various conditions (under irradiation by light from a mercury lamp, in daylight, or in the absence of illumination); this reaction leads to the formation of a low yield of asymmetric products—dialkoxythiophosphoryloxy—dialkoxyphosphorylthiomethanes:[155]

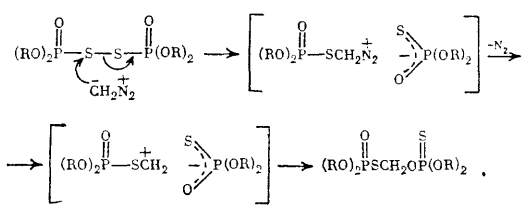


where R = alkyl.

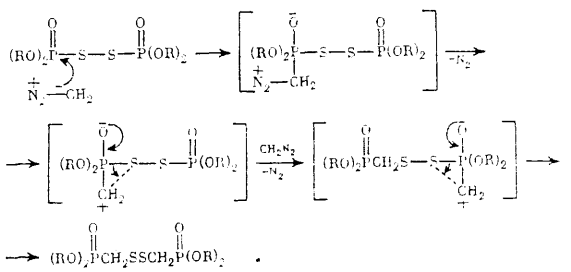
The ^{31}P NMR spectra of these compounds consist of two singlet signals with δ_P = 21–23.7 p.p.m. and 65.2–68.2 p.p.m., which are characteristic of quinquevalent phosphorus in the phosphoryl and thiophosphoryl groups respectively. The ^1H NMR spectra show a doublet of doublets due to the CH_2 group with δ_H = 5.28–5.40 p.p.m. ($^3J_{P(O)H}$ = 19.5 Hz, $^3J_{P(S)H}$ = 13.5 Hz), which also confirms the presence in the molecule of the phosphoryl and thiophosphoryl groups and the asymmetry of the structure formed. The infrared spectra contain an absorption band in the range 1260–1275 cm^{-1} (due to the vibrations of the P=O bond). The absorption band corresponding to the P=S group is shown in the Raman spectra in the range 615–630 cm^{-1}.[155]

Since the given reaction results in the formation of products containing the thiophosphoryl group instead of one of the initial phosphoryl groups, the reaction has been called the phosphoryl–thiophosphoryl rearrangement.[155]

It is believed that, at least in the absence of illumination, bis(dialkoxyphosphoryl) disulphides interact with an undissociated diazomethane molecule. This reaction can be represented by different schemes. One of these involves attack by diazomethane on one of the sulphur atoms with rupture of the disulphide bond and the formation of an intermediate structure with an ambident thiophosphoryl anion and a phosphorus-containing diazonium cation; the last species, which is an unstable intermediate, gives off nitrogen and is converted into the more stable phosphorus-containing carbonium ion, which attacks the rigid end of the triad, namely oxygen, in the $(O\therefore P\therefore S)^-$ ambident system:

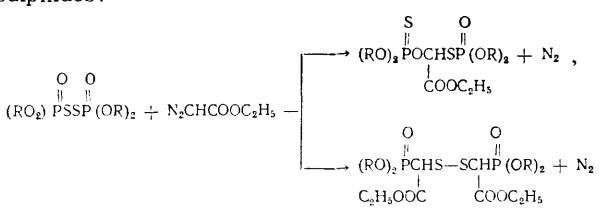


The interaction of bis(dialkoxyphosphoryl) disulphides with diazomethane in the absence of illumination is not restricted to the phosphoryl–thiophosphoryl rearrangement and is accompanied by the formation of the products of insertion of two methylene groups in both P–S bonds of the disulphide with retention of the S–S bond and the symmetry of the structure.[156] The formation of products of the P–S insertion has been represented by a scheme involving successive attack by diazomethane on the phosphorus atom of the disulphide with the intermediate formation of a dipolar diazonium ion, its decomposition to N_2 and a dipolar carbonium ion, and the 1,2-migration of the P(O)SS fragment to the carbonium centre; an analogous sequence of stages after the attack by a second diazomethane molecule leads to the final product:



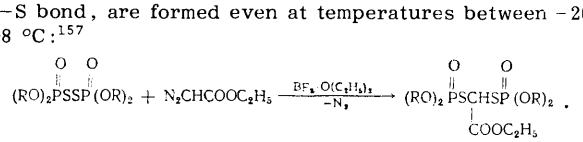
The ^1H NMR spectrum of the products of insertion in the P–S bond of the disulphide (R = iso-C_3H_7) contains a doublet associated with the methylene protons of the CH_2 group having δ_H = 2.21 p.p.m. ($^2J_{PH}$ = 15 Hz). The $^{31}P-\{^1H\}$ NMR spectrum consists of a singlet with δ_P = 24.9 p.p.m.; the infrared spectrum contains an absorption band due to the P=O group in the region of 1260 cm^{-1}.[156]

The interaction of bis(dialkoxyphosphoryl) disulphides with diazoacetic ester involves (as in the reaction with diazomethane) under conditions not promoting the formation of a carbene, involves both the phosphoryl–thiophosphoryl rearrangement with formation of dialkoxythiophosphoryloxy-dialkoxyphosphorylthioacetic esters and the insertion of the ethoxycarbonylmethylene group in both P–S bonds with formations of bis(ethoxycarbonyldialkoxyphosphonomethyl) disulphides:[156]



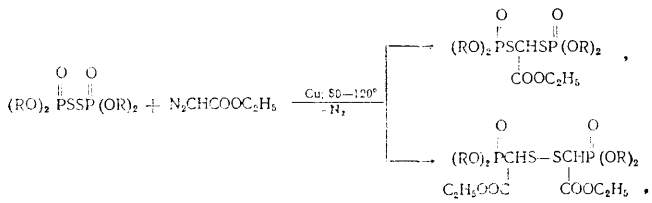
The two competing reactions take place at different rates and, depending on the process conditions, it is therefore possible to obtain each reaction product separately or their mixture in different proportions.

The reaction under the conditions of the catalytic generation of ethoxycarbonylcarbene leads to different results. When bis(dialkoxyphosphoryl) disulphides react with diazoacetic ester in the presence of catalytic amounts of boron trifluoride etherate, bis(dialkoxyphosphorylthio)acetic esters, the products of the insertion of ethoxycarbonylcarbene in the S–S bond, are formed even at temperatures between –20° and +8 °C:[157]

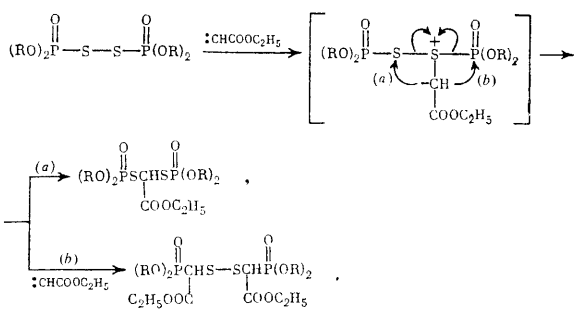


The ^1H NMR spectra of these compounds contain a triplet due to the methylidyne proton of the $CHCOOC_2H_5$ group with δ_H = 4.90–5.04 p.p.m. ($^3J_{PH}$ = 13.5 Hz). A singlet with δ_P = 21.1–21.6 p.p.m. can be observed in the $^{31}P-\{^1H\}$ NMR spectra. The infrared spectra contain absorption bands corresponding to the stretching vibration frequencies of the P=O (1265–1275 cm^{-1}) and C=O (1745 cm^{-1}) bonds.[157]

Under the conditions of the catalytic generation of the carbene in the presence of copper powder at 80 °C in benzene or at 80–120 °C in the absence of the solvent, the formation of the product of the insertion of ethoxycarbonylcarbene in the S–S bond of the disulphide is accompanied by the competing reaction involving insertion in both P–S bonds:[157]

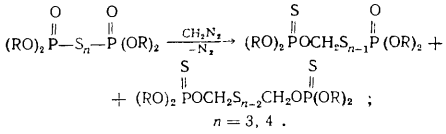


The insertion of ethoxycarbonylcarbene in the S–S bond apparently proceeds via a stage involving the formation of an unstable sulphonium ylide with subsequent 1,2-migration of the phosphorylsulphenyl group from the sulphonium sulphur atom to the ylide carbon atom (pathway *a*). The insertion of ethoxycarbonylcarbene in the P–S bond is also regarded as a process involving the intermediate formation of a sulphonium ylide with subsequent migration of the phosphoryl group from the sulphonium sulphur atom to the ylide carbon atom (pathway *b*):[157]

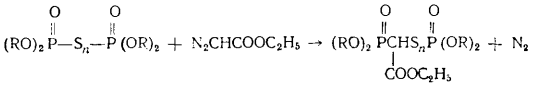


Since insertion in the P–S bond is observed also under conditions which do not promote the formation of carbenes, it is necessary to take into account the possibility of the reaction with an undissociated molecule of the diazo-compound. However, in this case the reaction centre is apparently the phosphorus atom and not the sulphur atom in the disulphide molecule.

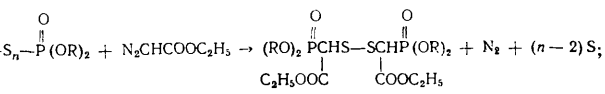
Phosphorus-containing tri- and tetra-sulphides form the products of the phosphoryl–thiophosphoryl rearrangement on interaction with diazomethane:[158]



In the reaction with diazoacetic ester there is no rearrangement and the products of the insertion of the ethoxycarbonylmethylene group in one of the P–S bonds of the polysulphide are formed in a high yield:[159]

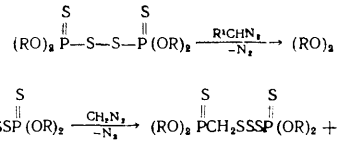


In the presence of an excess of diazoacetic ester, two ethoxycarbonylmethylene groups are inserted in the P–S bonds of the polysulphides and desulphurisation takes place:[159]



$n = 3, 4$.

Reactions analogous to those described above have also been considered in relation to thiophosphoryl di-, tri-, and tetra-sulphides:[160–162]

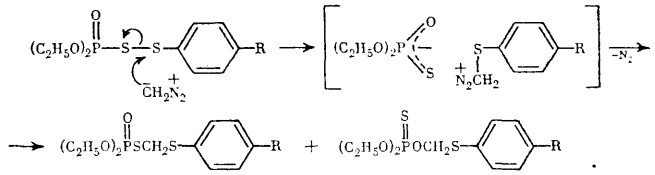


where R = alkyl and R′ = H or $COOC_2H_5$.

In the case of bis(dialkoxythiophosphoryl tetrasulphides the sequence of the insertions of the methylene group initially in one and then in the other S–S bond of the polysulphide has been observed with the aid of ^1H NMR spectroscopy. This is indicated by one doublet due to the protons of the CH_2 group with $\delta_H = 4.02$ p.p.m. ($^3J_{PH} = 18$ Hz), appearing initially in the spectrum, and then by the second doublet with $\delta_H = 3.75$ p.p.m. ($^3J_{PH} = 18$ Hz).[162]

It has been suggested that the phosphoryl–thiophosphoryl rearrangement takes place in the reaction with an undissociated molecule of the diazo-compound, while the S–S insertion is a reaction of the carbene type. The P–S insertion reaction can apparently be both of the carbene and non-carbene types.

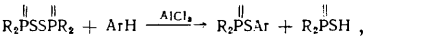
As regards phosphorus-containing disulphides with an asymmetric structure, it has been reported that the methylene group is inserted in the S–S bond of aryl diethoxyphosphoryl disulphide in its interaction with diazomethane.[95] The products of the rearrangement were obtained in an insignificant yield.[166] It is believed that the formation of arylthiodiethoxyphosphorylthiomethane and arylthiodiethoxythiophosphoryloxymethane proceeds via the "diazonium" mechanism; the diazonium cation interacts with the thiophosphoryl anion to a greater extent via the sulphur atom and to a lesser extent via the oxygen atom of the ambident $(O\cdots P\cdots S)^-$ triad:[166]



The reactions of phosphorus-containing polysulphides with diazo-compounds make it possible to obtain organophosphorus compounds which had been difficult to synthesise otherwise or had been altogether unknown and lead to interesting possibilities for the study of the carbene reactions in the chemistry of organophosphorus compounds.

10. The Reactions of Phosphorus-containing Disulphides in the Presence of Lewis Acids

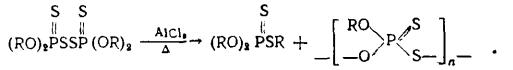
When phosphorus-containing disulphides react with aromatic hydrocarbons and alkyl aryl ethers in the presence of Lewis acids, the corresponding S-aryl esters of phosphorothioic acids are formed:[167,168]



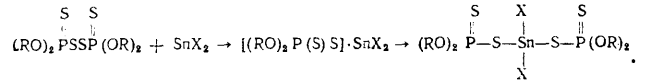
where R = alkoxy-group or phenyl. One must note that, in the case where the unsubstituted alkyl aryl ethers are employed, a mixture of isomers is formed whose separation presents certain difficulties.

When bis(dialkoxythiophosphoryl) disulphides are used, alkylation of the aromatic ring is also observed and in some cases this reaction predominates.[167,168]

In the presence of Lewis acids, bis(dialkoxythiophosphoryl) disulphides are capable of self-alkylation:[167]



The interaction of phosphorus-containing disulphides with tin dihalides is of interest:[169,170]



A complex of tin dihalide is apparently formed initially. The subsequent redistribution of electron density leads to the rupture of the S–S bond and the formation of S–Sn valence bonds.

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Thus the unusual chemical behaviour of phosphorus-containing polysulphides renders this group of compounds extremely promising for use in organic synthesis in order to obtain new types of organophosphorus compounds or compounds of this kind which have been hitherto difficult to obtain.

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All-Union Institute of Chemical
Plant Protecting Agents, Moscow

Translated from *Uspekhi Khimii*, 53, 1352-1379 (1984) U.D.C. 547.3:542.97+541.138

Oligomerisation Reactions of Vinyl Monomers Containing Functional Groups

V.P.Yur'ev, G.A.Gailyunas, and O.T.Kofanova

The results of studies on the oligomerisation reactions of vinyl monomers containing functional-group substituents using metal-complex catalytic systems and thermal and electrochemical methods are surveyed. The chemical reaction mechanisms are examined.
The bibliography includes 127 references.

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I. INTRODUCTION

The oligomerisation and co-oligomerisation reactions of α-olefins and 1,3-dienes, whereby it is possible to obtain a series of linear and cyclic products of potential interest to various branches of industry, have been thoroughly investigated and extensively described in the literature. The mechanisms and kinetics of these reactions, occurring in the presence of metal-complex catalytic systems, have been established.

The behaviour of olefins containing functional groups in reactions of this kind has not been studied quite so widely. Nevertheless the presence of a polar substituent in the olefin molecule alters the electron density in the double bond and is reflected in the course of the oligomerisation process.

In the present review an attempt has been made to survey the available literature data on the oligomerisation of vinyl monomers with functional groups and also on their co-oligomerisation with olefins, dienes, and trienes.

The vinyl monomers with functional groups consist mainly of α,β-unsaturated nitriles and esters as well as vinyl derivatives of silicon.

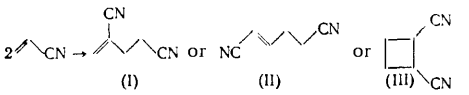
The possibility of the successful oligomerisation and co-oligomerisation of these compounds in the presence of metal-complex catalytic systems to form polyfunctional products containing a definite number of units of the initial monomer in the molecule has been demonstrated. Many of them can be of definite interest for industrial use and some are already manufactured in fairly large quantities.

The data presented in this review may prove useful in the selection of catalysts and reaction conditions ensuring high yields of the required block polymers based on vinyl monomers with functional-group substituents.

II. OLIGOMERISATION OF VINYL MONOMERS

1. Oligomerisation of Acrylonitrile

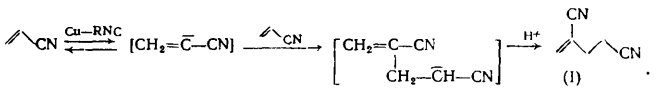
Depending on the selected conditions, the oligomerisation of acrylonitrile leads to the formation of linear dimers [α-methyleneglutaronitrile (I) and 1,4-dicyanobut-1-ene (II)], cyclic dimers [*cis*- and *trans*-1,2-dicyanocyclobutanes (III)], and higher oligomers (tri-, tetra-, and hexa-mers, etc.); the latter are formed as a rule in comparatively small amounts as admixtures to the dimeric products:



Dicyanocyclobutanes (III) are formed on thermal and photochemical cyclodimerisation of acrylonitrile. Thus, when acrylonitrile is heated to 200–300 °C, a mixture of cyclic dimers (III) is obtained in a yield of 2.5% of theoretical.[1] Approximately 4% of 1,2-dicyanocyclobutanes are formed in the photoinitiated dimerisation of acrylonitrile in the presence of sensitisers—benzophenone, 9,10-dibromoanthracene, xanthone, and others.[2] The same yield of cyclic dimers has been obtained as a result of photodimerisation in the presence of copper monochloride, which forms an intermediate coordination complex with acrylonitrile.[3] A 10% degree of conversion of acrylonitrile into 1,2-dicyanocyclobutanes has been achieved by carrying out photochemical dimerisation in the presence of molybdenum or tungsten carbonyls and reaction promoting agents, for example, triphenylphosphine.[4]

The selective formation of the linear dimer (I) has been observed in the dimerisation of acrylonitrile in the presence of binary catalytic systems consisting of copper, iron, or cobalt acetylacetonate and t-butyl- or cyclohexylisonitrile, but cyclohexylisonitrile can be used only in combination with copper and cobalt acetylacetonates, since in the presence of iron compounds it begins to polymerise appreciably lowering the catalytic activity of the system.[5,6] An obligatory condition is the presence of a proton-donating solvent, for example, a mixture of t-butyl alcohol with acetonitrile In the absence of a solvent acrylonitrile polymerises almost completely in the presence of catalytic systems of this kind. It is noteworthy that isonitrile–copper(I) oxide systems are inactive in the oligomerisation reactions of acrylonitrile.

The proposed mechanism of the dimerisation of acrylonitrile in the presence of metal–isonitrile systems involves the formation of intermediate carbanionic complexes whose existence has been confirmed by deuterium exchange reactions:[5]



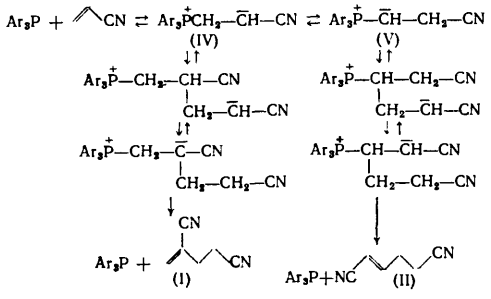
The dimerisation proceeds fairly slowly (20 h is required to obtain appreciable yields at 110 °C). The yield of the dimer (I) depends on the composition of the catalyst and reaches 50–52%.

α-Methyleneglutaronitrile is obtained in high yields (up to 68–72%) when two-component catalytic systems incorporating organic or inorganic zinc, cobalt, chromium, and aluminium salts, as well as nitrogen-containing Lewis bases (tertiary amines containing aliphatic, alicyclic, and aromatic groups or heterocyclic amines) are used.[7–11] The reaction proceeds at 20–70 °C. A small amount of the trimer (2,4,6-tricyanohex-1-ene) was found in the reaction products.

A mixture of the linear dimers (I) and (II) is formed on dimerisation of acrylonitrile in the presence of phosphorus(III) compounds.[12–31] The ratio of the isomers depends to a large extent on the nature of the organophosphorus compounds and on the solvent, temperature, and other factors. A degree of conversion of acrylonitrile not exceeding 7–9% has been achieved in dimerisation in the presence of tributyl- and triphenyl-phosphines at 45–50 °C.[12] The formation of the dimers was accompanied by the appearance of considerable amounts of the trimer (1,3,5-tricyanohex-1-ene), the hexamer, and other oligomers. The acrylonitrile hexamer 3,6-di(cyanoethyl)-1,3,6,8-tetracyano-*trans*-oct-4-ene was first detected in the oligomerisation of acrylonitrile in the presence of triphenylphosphine at 80 °C in the course of 2–4 weeks.[32]

The study of the dimerisation of acrylonitrile in the presence of triarylphosphines at 160–175 °C led to an increase in the degree of conversion of acrylonitrile to 36% and of the yield of the dimers to 85% (relative to the monomer which has reacted).[19,20] Best results have been obtained using tri(*p*-tolyl)phosphine as the catalyst. The higher nucleophilicity of methyl-substituted triarylphosphines compared with triphenylphosphine not only increases the degree of conversion of acrylonitrile but also reduces the content of the isomer (II) in the mixture of dimers from 39 to 30–32%. In dimerisation in the presence of the still more nucleophilic tri(*p*-anisyl)phosphine, the content of compound (II) falls to 9%.

The proposed mechanism of the dimerisation of acrylonitrile in the presence of tertiary phosphines includes the formation of two types of intermediate species—the phosphonium-substituted carbanion (IV) and the phosphorus ylide (V); the reactions of these species lead to the formation of α-methyleneglutaronitrile (I) and 1,4-dicyanobut-1-ene (II) respectively:[12,20]



The choice of the proton-donating solvent for the dimerisation reaction merits special attention. On passing from t-butyl alcohol to triethylsilanol, which exhibits a higher protolytic activity, the yield of the dimers increases by 20–30% other conditions being equal.[20] The absence of a source of protons promotes chain propagation and the formation of higher oligomers. In order to suppress the polymerisation reaction, it is recommended that inhibitors, namely hydroquinone, t-butylcatechol, phenothiazine, and others, be added to the reaction mixture.

A high yield of α-methyleneglutaronitrile (99%) and a satisfactory degree of conversion of acrylonitrile (up to 40%) have been achieved by carrying out continuous dimerisation in a cascade of three reactors in the presence of tri(cyclohexyl)phosphine at 80-140 °C. A mixture of t-butyl alcohol and benzene was employed as the solvent.[17]

The selective conversion of acrylonitrile into 1,4-dicyanobut-1-ene(II) takes place in the presence of catalytic amounts of the phosphonites $XArP(OR)_2$ and the phosphinites $(XAr)(Ar)POR$ or $(XAr)_2POR$, where R = alkyl or cycloalkyl, Ar = phenyl or naphthyl, and X is an electron-donating substituent: an alkyl, alkylamino-, or alkoxy-group.[25–31]

It is recommended that in this instance the dimerisation of acrylonitrile be carried out at low temperatures (below 75 °C) in the presence of a proton-donating alcoholic solvent mixed with an aprotic hydrocarbon cosolvent. An obligatory condition which must be observed to ensure a high rate of dimerisation is the employment of absolutely dry reagents and solvents, since moisture reacts with the catalyst, forming inactive compounds. When the catalyst and the mixed solvent are chosen correctly, the yield of the linear dimer (II) is 85–89% for a degree of conversion of acrylonitrile of 66–75%.[30]

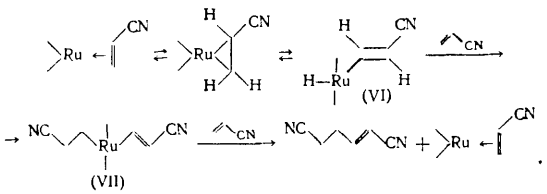
In the presence of bismuth compounds ($BiCl_3$, Bi_2O_3, $BiPh_3$, etc.) a high selectivity is achieved in the formation of 1,4-dicyanobut-1-ene (80%), but the degree of conversion of acrylonitrile is low (1–2.5%).[33] It has proved possible to enhance the catalytic effect of bismuth by adding the compounds of other metals (Sb, Co, Rh, Ir, and Ru), as a result of which the degree of conversion of acrylonitrile increases to 18%.[34–37]

The preferential formation of 1,4-dicyanobut-1-ene(II) has been observed in the dimerisation of acrylonitrile in the presence of catalytic systems containing ruthenium.[38–47] Apart from ruthenium chloride, which has come to be most widely used, the ruthenium salts of inorganic and organic acids or ruthenium complexes can be used as the main component of the catalysts. In order to accelerate the reaction and suppress the formation of side products, some workers recommend the addition of promoting agents—compounds of copper, silver, palladium, cadmium, tin, alkali metals, and alkaline earth metals.

Hydrogen plays an important role in the reaction. In the absence of hydrogen, the dimerisation of acrylonitrile in the presence of ruthenium catalysts hardly occurs. The role of hydrogen is explained by its involvement in the formation of a ruthenium hydride complex, which interacts with acrylonitrile to form the cyanoethyl complex $>Ru-CH_2-CH_2-CN$. The insertion of a second acrylonitrile molecule in the Ru–C bond leads to the dicyanobutylruthenium complex $>Ru-\underset{CN}{CH}-CH_2-CH_2-CH_2-CN$, which decomposes with liberation of 1,4-dicyanobut-1-ene. The main reaction is accompanied by the appearance of fairly large amounts of propionitrile (about 50%) and adiponitrile (up to 4%)—the products of the reaction of the cyanoethyl- and dicyanobutyl-ruthenium complexes with hydrogen.[38]

The study of the dimerisation of acrylonitrile in the presence of ruthenium catalysts in a deuterium atmosphere suggested a reaction mechanism involving the intermediate formation of the catalytically active cyanovinylruthenium hydride complex (VI) as a result of the insertion of the metal in the vinyl carbon–hydrogen bond. The interaction of the complex (VI) with a second acrylonitrile molecule leads

to the dimeric complex (VII), which decomposes with formation of 1,4-dicyanobut-1-ene and the regeneration of the catalyst:[48]

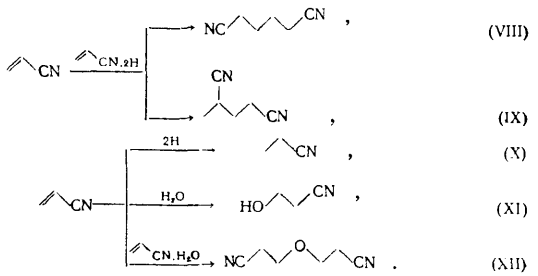


In the absence of hydrogen but in the presence of added electron-donating ligands, which form a coordinate bond with ruthenium (amines, carboxylic acids and their salts), the acrylonitrile dehydrodimerisation products—a mixture of the geometrical isomers of 1,4-dicyanobuta-1,3-diene—are formed preferentially.[49] Equimolar amounts of 1,4-dicyanobuta-1,3-diene and propionitrile have been obtained on dimerisation of acrylonitrile in the presence of catalytic platinum complexes incorporating diethylamine ligands: $(C_2H_4)Pt.(Et_2NH)Cl_2$ and $Et_2NHCH_2CH_2Pt(Et_2NH)Cl_2$.[50]

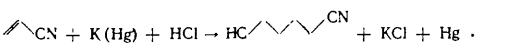
The acrylonitrile hydrodimer, namely adiponitrile (VIII), merits special attention, because it is one of the monomers used in the large-scale manufacture of nylon-6,6. Apart from the dimerisation reaction, already mentioned above, of acrylonitrile in the presence of ruthenium catalysts in an atmosphere of hydrogen, where adiponitrile is formed as an admixture to the main product (1,4-dicyanobut-1-ene),[38,51-53] it can be obtained in a mixture with another hydrodimer, namely 2-methylglutaronitrile (IX), on dimerisation of acrylonitrile in the presence of catalytic systems of three types containing iron and cobalt carbonyls:

$$Fe(CO)_5 \text{ or } Co_2(CO)_8 + \text{alkali} + H_2O;$$
$$Fe(CO)_5 \text{ or } Co_2(CO)_8 + NaBH_4 \text{ or } LiAlH_4;$$
$$Co_2(CO)_8 + H_2.$$

It is recommended that the reaction be carried out at 110 °C at a pressure of 80 atm in benzene or methanol with addition of a polymerisation inhibitor.[54] In all cases appreciable amounts of propionitrile (X) are formed in addition to the hydrodimers. In aqueous media acrylonitrile reacts partly with water to form ethylenecyanohydrin (XI) and biscyanoethyl ether (XII):



A satisfactory yield (90–100%) of adiponitrile has been achieved by dimerising acrylonitrile in the presence of Co(O) complexes, in particular $Co(N_2)(PPh_3)_3$.[55] The possibility of the selective hydrodimerisation of acrylonitrile to adiponitrile using an alkali metal amalgam has been reported:[56-58]

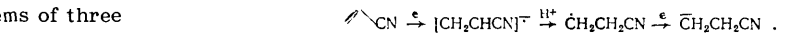


This well known method, used in preparative organic chemistry, has been tested on large-scale experimental apparatus. The course of the reaction is greatly influenced by the stability of the intermediate free radicals, the radicals generated on the surface of the amalgam being more stable than those in solution; the polymerisation of acrylonitrile is therefore not observed in this process. The yield of adiponitrile in the first runs was 60–62% and was later increased to 85–90% relative to the acrylonitrile which has reacted and finally more than 95% of adiponitrile was obtained in a polar solvent—acetonitrile with added water and a quaternary ammonium salt. The main reaction is accompanied by the appearance of small amounts of propionitrile.[58]

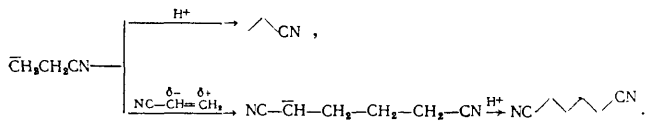
The formation of a side product (alkali metal chloride) and the high consumption of the amalgam must be regarded as disadvantages of the amalgam method for the hydrodimerisation of acrylonitrile. Studies are therefore being continued in order to improve the amalgam method and to replace potassium amalgam by the cheaper sodium amalgam, which is formed in large amounts as an intermediate in the manufacture of chlorine from caustic soda by the electrolysis of common salt. The successful completion of these studies will make it possible to combine the manufacture of adiponitrile with the electrolysis of common salt and thus ensure the supply of cheap adiponitrile.

A convenient method for the synthesis of dimeric products from the initial unsaturated compounds is that of direct cathodic hydrodimerisation. This method has been fairly extensively developed and the cathodic hydrodimerisation of acrylonitrile with formation of adiponitrile has been achieved on the industrial scale.[58-60]

In the first stage of the process a radical-anion is formed at the cathode and then rapidly transformed into a carbanion:



At a comparatively high pH of the aqueous solution and high acrylonitrile concentrations the carbanion undergoes nucleophilic addition to a second monomer molecule, forming a dimeric carbanion, which is protonated to give adiponitrile. At a low pH (less than 2) and low acrylonitrile concentrations (less than 10%) the carbanion is protonated with formation of propionitrile:



In anhydrous electrolytes higher acrylonitrile oligomers are formed.

In order to increase the yield of adiponitrile and suppress the formation of side products, it is necessary to maintain the acrylonitrile concentration in the electrolyte above 10%. With the aim of increasing the electrical conductivity and solubility of acrylonitrile, the hydrodimerisation is carried out in a solution of a quaternary ammonium salt (tetraethylammonium toluene-p-sulphonate) or in a mixture of aqueous solutions of potassium phosphate and tetraethylammonium phosphate.

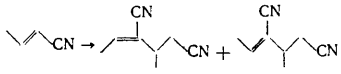
The reaction is carried out at 25–50 °C at lead or graphite cathodes using a current density of 25–100 A dm^{-2} (lead) or 4–15 A dm^{-2} (graphite). The yields with respect to the test substance and the current reach 90–93%.

The electrochemical method of synthesis of adiponitrile competes successfully with the chemical methods, which are employed under more severe conditions. At the present time industrial and large experimental plants for the electrochemical hydrodimerisation of acrylonitrile, operating in the USA, England, Japan, Belgium, and the Federal Republic of Germany, produce more than 170000 tonnes of adiponitrile

annually and the unit capacity of the plants has been raised to 90000 tonnes per annum.

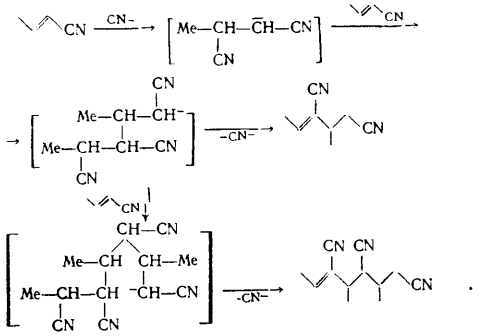
2. The Oligomerisation of α(β)-Alkyl-substituted αβ-Unsaturated Nitriles

Few studies have been devoted to the oligomerisation of αβ-unsaturated nitriles substituted in the β-position. In the investigation of the dimerisation of αβ-unsaturated carbonyl compounds and nitriles in the presence of binary catalytic systems comprising copper(I) and copper(II) compounds and isonitriles considerable attention has been devoted to the dimerisation of crotononitrile, which results in the formation of a mixture of geometrical isomers of 1,3-dicyano-2-methylpent-3-ene: [5,61]



In contrast to acrylonitrile, the dimerisation of crotononitrile proceeds readily in the presence of copper(I) oxide–t-butyl- or cyclohexyl-isonitrile systems without the need for the presence of proton-donating solvents (acrylonitrile polymerises under these conditions). At 90 °C the yield of crotononitrile dimers in the presence of such systems reaches 90% after only 1 h. [61] Copper acetylacetonate and chloride as well as copper(II) oxide can also be employed for the dimerisation of crotononitrile, but they are less active. It is of interest that the copper compound—isonitrile systems are effective only when the substituent in the β-position is a primary or secondary alkyl group. Compounds with a tertiary alkyl or aryl group in the β-position do not dimerise.

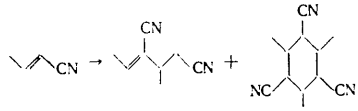
The crotononitrile dimer has been obtained in 52–54% yield together with a mixture of trimers in 33% yield in the oligomerisation of crotononitrile in the presence of tetraalkylammonium cyanides, in particular $(Et_4N)_3[Co(CN)_5]$ and $(Et_4N)_3[Co(CN)_5O_2]$. The more reactive acrylonitrile is fully polymerised in the presence of catalysts of this type. The mechanism of the oligomerisation of crotononitrile has been formulated as follows: [62]



The prolonged (up to 2 h) induction period when tris(tetraethylammonium) pentacyanocobaltates are used could not be accounted for.

Crotononitrile also oligomerises when yet another nucleophilic anionic cobalt(I) complex is employed, namely cobalt N,N′-ethylenebis(salicylideneiminate). [63] The use of this complex in the form of the sodium salt im dimethylformamide leads to the formation of the dimer (1,3-dicyano-2-methylpent-3-ene) in 68% yield and the trimer (1,3,5-tricyano-2,4-dimethylhept-5-ene) in 20% yield. In this case too acrylonitrile gives rise to a solid polymer and a small amount of α-methyleneglutaronitrile is formed only after the addition of t-butyl alcohol (a weak proton donor) (the yield of the acrylonitrile dimer is ~50 times smaller than that of the crotononitrile dimer). According to the author, acrylonitrile promotes the conversion of the active univalent cobalt complex into an inactive bivalent cobalt compound.

In the presence of the potassium–benzylpotassium catalytic system the oligomerisation of crotononitrile results in the formation of the dimer (1,3-dicyano-2-methylpent-3-ene) and a cyclic trimer (1,3,5-tricyano-2,4,6-trimethylcyclohexane): [64]



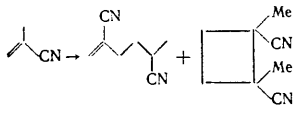
The reaction is carried out in the presence of an excess of toluene or methylcyclohexane at 110 °C. After 1 h, the degree of conversion of crotononitrile reaches 88.5%. The yield of the mixture of *cis*- and *trans*-1,3-dicyano-2-methylpent-3-enes (in proportions of 67 : 33) is 20–23%, while that of the trimer is 67–75%. When potassium is replaced by sodium, the yield of the oligomerisation products is reduced to 30–35%, other conditions being equal, although the ratio of the dimer and trimer remains unaltered.

The data presented permit the conclusion that the dimerisation of β-alkyl-substituted αβ-unsaturated nitriles requires the presence of powerful nucleophiles. The latter induce the polymerisation of acrylonitrile, but weaker nucleophilic catalysts can be used to achieve its dimerisation.

Several studies have been devoted to the oligomerisation of methacrylonitrile. A patent, [10] in which the oligomerisation of acrylonitrile is considered in detail, mentions the possibility of the oligomerisation of methacrylonitrile in the presence of catalytic systems comprising the zinc or cobalt salts of trifluoromethanesulphonic acid and triethylamine, but there are no data concerning the composition and yield of the oligomerisation products and also the degree of conversion of the initial monomer.

The possibility of obtaining α-methylene-δ-methylaldipodinitrile (a linear methacrylonitrile dimer) in the presence of a mixed catalyst containing α- or β-naphthylamine and $NiCl_2$ has been investigated. [65] The reaction is carried out at 220–230 °C. Apart from the main product, small amounts of the cyclic dimer (1,2-dicyano-1,2-dimethylcyclobutane) and a trimer, whose structure is not given by the authors, are formed under these conditions.

When methacrylonitrile is heated in the presence of polymerisaton inhibitors, a mixture of α-methylene-δ-methyladipodinitrile with cyclic dimers (*cis*- and *trans*-1,2-dicyano-1,2-dimethylcyclobutanes) is formed: [66]



Large amounts of a trimer and higher oligomers have also been detected in the reaction products. As the reaction temperature is altered, the ratio of oligomers of different structure changes within wide limits. At 340 °C the fraction of the linear dimer is about 50% of the reaction products, while at 200 °C the cyclic isomers predominate in the reaction mixture.

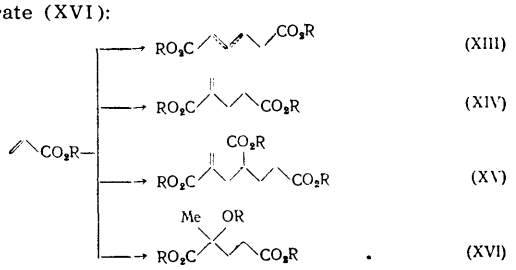
The cyclic methacrylonitrile dimer is formed in a very low yield (2%) as a result of the photodimerisation of methacrylonitrile in the presence of univalent copper. [3] Copper(I) chloride, which is readily soluble in the initial monomer, forms a coordination complex with the latter, ensuring the activation of the double bond and promoting ring closure.

The concentration of CuCl in methacrylonitrile should be not less than 8×10^{-3} M, since otherwise methacrylonitrile begins to polymerise.

Thus the oligomerisation reactions of unsaturated nitriles make it possible to obtain mainly linear dimers whose composition depends on the catalyst employed and the selected reaction conditions. Best results have been obtained using the electrochemical method for the hydrodimerisation of unsaturated monomers with functional groups.

3. The Oligomerisation of Alkyl Esters of Acrylic Acid

The oligomerisation of alkyl acrylates yields mainly three isomers: dialkyl Δ^2- or Δ^3-dihydromuconates (XIII) and dialkyl α-methyleneglutarate (XIV). In certain cases the dimerisation is accompanied by the formation of small amounts of the linear trimer (XV) and dialkyl α-alkoxy-*d*-methylglutarate (XVI):



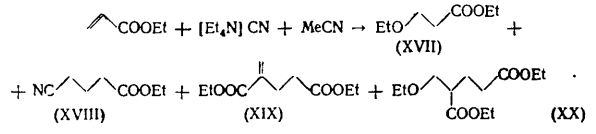
When copper–isonitrile binary systems are used, methyl acrylate is less reactive than acrylonitrile and significant results (yields of the dimer of 11%) are obtained only in the presence of the copper(I) oxide—isonitrile system and a proton-donating solvent. Without the solvent, the monomer polymerises very slowly and, when copper(I) oxide is replaced by copper or cobalt acetylacetonate, the yield of dimethyl α-methyleneglutarate falls to 1–2%.[5]

An analogous picture is observed when binary systems consisting of aluminium or zinc halides and nitrogen-containing Lewis bases are used. In this case too alkyl acrylates proved to be inert. Whereas the yield of the acrylonitrile dimers exceeds 50% in the presence of such catalysts, methyl acrylate gives rise to only 5% of dimethyl α-methyleneglutarate under identical conditions.[8]

There have been a number of reports concerning the possibility of the dimerisation of alkyl acrylates in the presence of organophosphorus compounds.[67–69] In the experiments performed with a solution of ethyl acrylate in t-butyl alcohol in the presence of triphenylphosphine a very low degree of conversion of the initial monomer into a mixture of diethyl α-methyleneglutarate and diethyl Δ^2-dihydromuconate was observed even after two weeks at 40 °C.[12]

Diethyl α-methyleneglutarate has been obtained in 67% yield when ethyl acrylate was dimerised in the presence of tributylphosphine in acetonitrile at 40–45 °C.[67] When tris(ethoxycarbonylethyl)phosphine was used, the yield of the diester fell somewhat, but remained fairly high (47%). The only side product in these reactions is the trimer, formed in small amounts.

A complex mixture of oligomerisaton products is obtained when less active catalysts, namely tetra-alkylammonium cyanides, are used:[62]

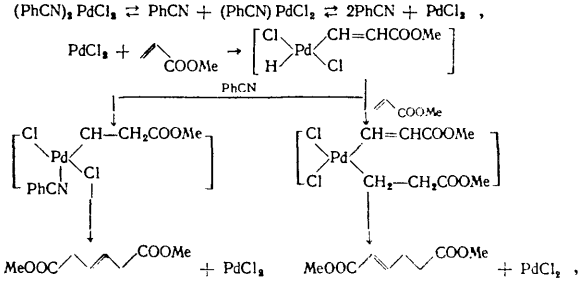


When the reactor is cooled to 5 °C, it is possible to obtain solely compounds (XVII) and (XX). Their formation shows that the ethoxy-group is displaced from the initial product under the reaction conditions with its subsequent addition to the activated double bond. The proton necessary for the formation of compound (XVII) is obtained following the Hoffmann cleavage of the tetraethylammonium cation. The yield of the dimer (XIX) is very low; compound (XVIII) is formed as a result of the addition of acetonitrile to the olefin via the Michael reaction, which the authors believe to be catalysed by the ethoxide anion (tetraethylammonium cyanides do not catalyse this reaction).

The anionic complex cobalt N,N'-ethylenebis-salicylideneiminate promotes the conversion of ethyl acrylate into diethyl α-methyleneglutarate with an insignificant admixture of the trimer.[63] After 10 h, the degree of conversion of the initial monomer reaches 40%. The anionic oligomerisation of methyl and ethyl acrylates has been investigated in the presence of sodium methoxide or ethoxide in anhydrous methanol and ethanol respectively.[70] In both cases the degree of conversion of the monomers is 80–90% after 24 h at the boiling point; in addition to dialkyl α-methyleneglutarate, the corresponding saturated alkoxy-derivative (XVI) was detected in the reaction products. It is noteworthy that in the case of ethyl acrylate the amount of unsaturated dimer obtained is greater than for methyl acrylate.

The preferential formation of dimethyl Δ^2-dihydromuconate is observed when ruthenium or rhodium trichloride trihydrate is used.[71] It is recommended that the reaction be performed in methanol or tetrahydrofuran. A temperature of 140 °C was sufficient for the attainment of a high yield of the dimer in the presence of $RhCl_3 \cdot 3H_2O$ and the formation of higher oligomers was not observed. $RuCl_3$ is less active in this reaction and 48% of the dimer was obtained only at 210 °C. The promoting influence of ethylene, whose addition makes it possible to reduce the reaction temperature to 150 °C and to increase the yield of the dimer to 56%, was unexpected Admittedly a small amount of methyl pent-3-enoate appears in the reaction products under these conditions as a result of the co-oligomerisation of ethylene with methyl acrylate.

Bivalent palladium complexes proved to be fairly active in the dimerisation reactions of alkyl acrylates.[72,73] The readily soluble, non-hygroscopic dichlorobisbenzonitrile complex, which catalyses the dimerisation of methyl acrylate in accordance with the mechanism



is very convenient for this purpose. After 23 h at 113 °C, the degree of conversion of methyl acrylate reaches 67% and the selectivity with respect to linear dimers exceeds 90%. The ratio of the Δ^2- and Δ^3-isomers varies in the range 50 : 50–67 : 33 depending on the reaction conditions.[72]

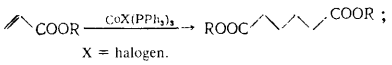
The high process selectivity led investigators to seek ways of increasing the effectiveness of palladium catalysts. The inadequate degree of conversion of alkyl acrylates (67%) is attributed to the comparatively rapid loss of activity by dichlorobis(benzonitrile)palladium.[74]

It was found that the addition of *p*-benzoquinone prevents not only the reductive deactivation of the catalysts but also the radical polymerisation of the monomer; the degree of conversion of the initial monomer increases to 75–92% and the necessary reaction temperature falls to 81 °C. It has been suggested that complexes more reactive than the initial complex may be formed between palladium phenoxide and the benzoquinone reaction products.[74]

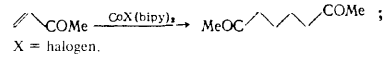
Silver tetrafluoroborate exerts an even stronger activating effect on the catalytic $PdCl_2$ complexes.[75] Depending on the catalyst/$AgBF_4$ ratio, the rate of dimerisation of methyl acrylate increases by 1–2 orders of magnitude and the selectivity changes in favour of dimethyl Δ^2-dihydromuconate. $AgBF_4$ has an analogous effect also on the dichlorophosphine-palladium complexes $(PhP)_2PdCl_2$ and $(Bu_3P)_2PdCl_2$, which hardly catalyse the dimerisation of alkyl acrylates in the absence of this additive. The activated complexes are especially selective and it is possible to obtain with their aid a virtually pure Δ^2-isomer (the admixture of dimethyl Δ^3-dihydromuconate does not exceed 1–3%).

It has been suggested that silver tetrafluoroborate promotes the formation of free coordination-unsaturated centres in the catalytically active complex as a result of the partial dissociation of the neutral ligand, which is confirmed by the impossibility of activating by $AgBF_4$ complexes containing chelating ligands such as 1,2-bis(diphenylphosphino)-ethane and 1,2-bis(N,N-dimethylamino(ethane.

In the presence of triphenylphosphine complexes of cobalt in protic solvents, alkyl acrylates undergo reductive dimerisation with formation of the corresponding dialkyl adipates:

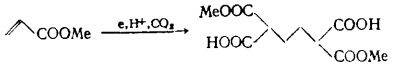


The hydrodimerisation of methyl vinyl ketone to octane-2,7-dione takes place successfully in the presence of cobalt complexes containing bipyridyl ligands:[76]



The electrochemical hydrodimerisation of alkyl acrylates, which takes place exclusively "tail to tail", is characterised by a high selectivity and satisfactory yields.[61,77] The yield of the hydrodimers depends on the composition of the electrolyte and the nature of the alkyl moiety in the ester group (it decreases with increased number of carbon atoms). Thus in an alkaline solution the yield of the methyl acrylate hydrodimer reaches 73%, while only 40% of diethyl adipate is formed from ethyl acrylate; in order to increase the yield of adipate to 75%, it is necessary to raise the electrical conductivity of the solution with the aid of quaternary ammonium salts. It has been altogether impossible to obtain the butyl acrylate hydrodimer by the electrochemical procedure.[77]

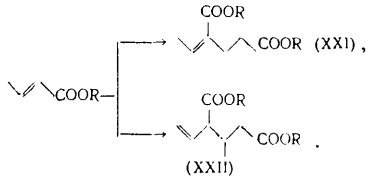
A very interesting product, namely the dimethyl ester of butane-1,1,4,4-tetracarboxylic acid, has been obtained in yields up to 47% by the electrochemical reduction of methyl acrylate in the presence of carbon dioxide:[78]



Great importance must be attributed to reactions of this type, since they lead to yet another possibility for the direct utilisation of carbon dioxide in organic synthesis.

4. Oligomerisation of the Alkyl Esters of Crotonic Acid

Depending on the catalyst, the oligomerisation of alkyl crotonates proceeds with formation of the dialkyl esters of 2-methylpent-3(or 4)-ene-1,3-dicarboxylic acid—compounds (XXI) and (XXII) respectively:



Some of the catalytic systems used for crotononitrile are suitable for these reactions. A mixture of the *cis*- and *trans*-isomers of compound (XXI) is formed from alkyl crotonates in the presence of the copper(I) oxide–cyclohexylisonitrile system in a fairly satisfactory yield (albeit lower than in the case of crotononitrile).[61,79] At 90 °C the yield of the methyl crotonate dimers reaches 70% after 3 h (the ratio of the *cis*- and *trans*-isomers in the mixture is 80 : 20). A characteristic feature is the need to employ a large excess of cyclohexylisonitrile relative to copper(I) oxide. When cyclohexylisonitrile is replaced by t-butylisonitrile, the reaction slows down (the yield of the dimers is only 50% after 12 h). Under these conditions, ethyl crotonate is more inert (the yield of the dimers does not exceed 15% after 14 h even at 100 °C).

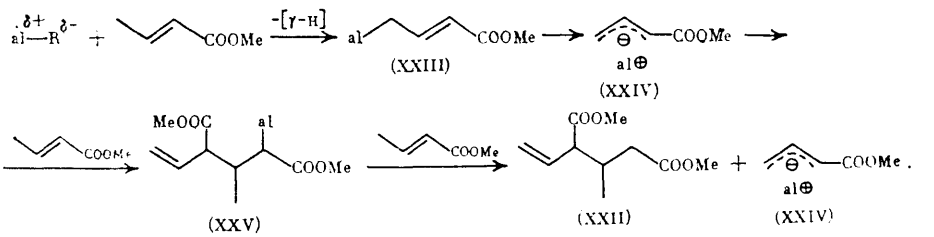
In the presence of tetraethylammonium cyanide in acetonitrile, ethyl crotonate dimerises with formation of 67% of the diethyl ester (XXI).[62]

Ethyl crotonate dimerises very rapidly and almost quantitatively at 110 °C in the presence of the potassium–benzylpotassium catalytic system in solution in toluene.[80] In contrast to crotononitrile, ethyl crotonate dimerises very selectively under these conditions—90% of the product consists of the dimer (XXI) and the content of the *cis*-isomer is higher than in the case of crotononitrile (81% instead of 67%).

A very pure dimethyl ester (XXII) has been obtained in a study of the oligomerisation of methyl crotonate in the presence of the trimethyl- or triethylaluminium–sparteine systems.[81,82] A mixture of compounds (XXI) and (XXII) in proportions of 11 : 73–54 : 34 (depending on the solvent employed) with an admixture of 12–16% of the diastereoisomers (XXII) is formed in the presence of the isobutylaluminium–sparteine system.

A mixture of compounds (XXI) and (XXII) in proportions of 97 : 3–69 : 31 has been obtained using the triethylaluminium–triethylamine catalytic complex; the content of the dimer (XXI) increases with reaction time, while the amount of compound (XXII) diminishes simultaneously, which shows that the dimer (XXI) is formed as a result of the isomerisation of compounds (XXII). It is noteworthy that acrylonitrile and methyl methacrylate polymerise fully in the presence of such catalytic systems.

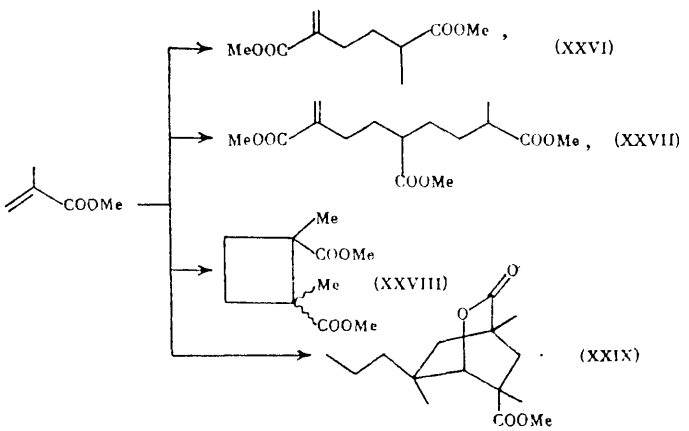
The author showed by experiments with methyl crotonate deuteriated in the α- and γ-positions that the reaction is initiated by the abstraction of the acid γ-proton from methyl crotonate by the catalytic complex and proposed the following reaction mechanism:



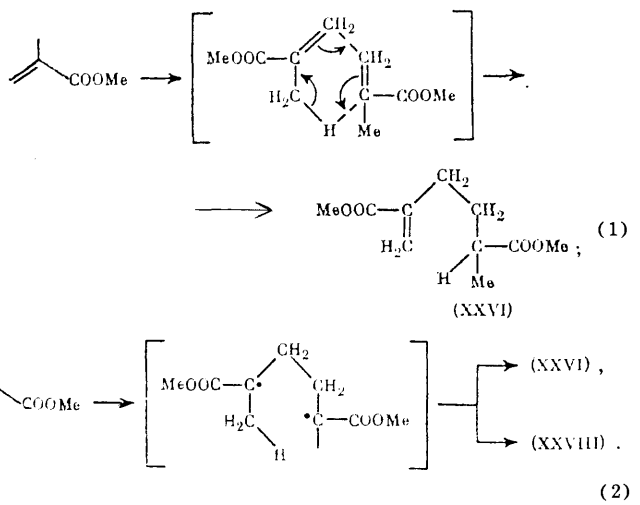
Here al represents the Et_2Al–sparteine residue. The abstraction of the γ-proton results in the formation of the intermediate complex (XXIII), which can have the delocalised structure (XXIV). This complex attacks the methyl crotonate molecule with formation of the adduct (XXV), which is converted into the dimer (XXII) with regeneration of the active complex (XXIV).

5. Oligomerisation of Alkyl Methacrylates

The esters of methacrylic acid and in the first place methyl methacrylate are known to be widely used in the manufacture of film-forming polymers. The appearance of oligomers of different structure in the course of the polymerisation of methacrylates stimulated investigators to study the conditions and mechanism of the formation of oligomers during the heat treatment of the alkyl esters of methacrylic acid. The probability of the formation of the following methyl methacrylate oligomers has been demonstrated: dimethyl 1-methylene-4-methyladipate (XXVI), trimethyl non-1-ene-2,5,8-tricarboxylate (XXVII), dimethyl *cis*- and *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylates (XXVIII), and a cyclic trimer—methyl 4,6,7-trimethyl-3-oxo-7-propyl-2-oxabicyclo[2.2.2]octane-6-carboxylate (XXIX):



In one of the early studies[66] it was shown that, when methyl methacrylate is heated for 12 h at 225 °C, mainly the linear dimer (XXVI) and the linear trimer (XXVII) are obtained. The same products have been synthesised by the thermal oligomerisation of methyl methacrylate at 100°, 120°, and 130 °C [83] (we may recall that an appreciable proportion of the methacrylonitrile reaction products consist of cyclic dimers under these conditions). Two possible dimerisation mechanisms have been considered: the "ene-enophilic" (1) and the biradical (2) mechanisms:



It has been suggested[83] that in the latter case chain termination and disproportionation of the biradical take place in the course of the reaction with formation of the linear dimer (XXVI) and that only a small proportion of the methacrylate cyclises to the tetrasubstituted cyclobutane (XXVIII).

However, on the basis of the study of the kinetics of this process, it was concluded that the formation of compound (XXVIII) agrees with the biradical initiation mechanism, while the linear dimer and trimer are obtained via the "ene-enophilic" mechanism.[84]

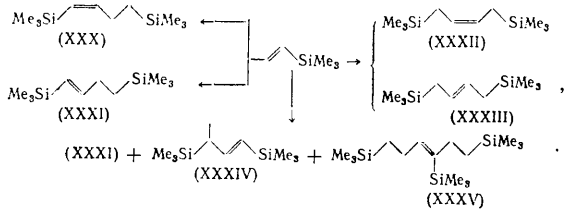
The methyl methacrylate trimer, obtained under the influence of diethylaluminium chloride in the presence of 2,2'-azobisisobutyronitrile as the initiator, has been identified as the bicyclic lactone (XXIX).[85]

6. Oligomerisation of Vinyl Derivatives of Silicon

The oligomerisation of vinyl derivatives of silicon with formation of di-, tetra- and octa-mers was first mentioned in connection with the study of the polymerisation of these monomers.[86,87] The specific synthesis of the linear dimers of trimethylvinyl- and triethylvinyl-silanes was achieved in 1961 by the reaction of the monomers with triisobutylaluminium.[88] For a number of years no studies on these lines were performed and it is only recently that reports have appeared concerning the results of the investigation of the oligomerisation of vinylsilanes in the presence of metal complex systems.[89,90]

Three-component systems consisting of nickel, cobalt, or titanium compounds, as organoaluminium reductant, and triphenylphosphine or triphenylstibine as the electron-donating additive have been investigated. The nickel and cobalt compounds have been used as chelates and the titanium compound was tetrabutoxytitanium. In the

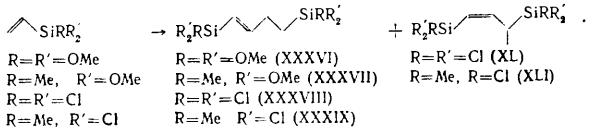
presence of such metal complex catalysts trimethylvinylsilanes give rise mainly to disilylbutenes with different configurations and with different positions of the double bond:



In the presence of the system prepared by treating cobalt 8-hydroxyquinolate with triethylaluminium in the presence of triphenylphosphine, trimethylvinylsilane dimerises with formation of 1,4-bis(trimethylsilyl)-*cis*-but-1-ene (XXX) in 30% yield relative to the monomer which has reacted. The replacement of triphenylphosphine by triphenylstibine leads to the formation of the *trans*-isomer (XXXI) in the same yield. The metal complex system comprising nickel acetylacetonate, triethylaluminium, and triphenylphosphine in the absence of a solvent showed no catalytic activity in relation to vinylsilanes, but the use of dichloroethylene as the solvent led to the formation of a mixture of compounds (XXXII) and (XXXIII) in proportions of 1:1 and in 86% yield. When the organoaluminium reductant is replaced by trichlorosilane, the dimer (XXX) is obtained in 30% yield.

Whereas the nickel and cobalt catalysts make it possible to obtain only unbranched trimethylvinylsilane dimers, the system comprising tetrabutoxytitanium, triethylaluminium and triphenylphosphine promotes the formation of the branched dimer *trans*-1,3-bis(trimethylsilyl)-3-methylprop-1-ene (XXXIV) together with the linear dimer (XXXI). In addition the formation of the linear trimer 1,2,3-tris(trimethylsilyl)hex-3-ene (XXXV) has been noted. The oligomers are formed in the proportions (XXX):(XXXIV):(XXXV) = 2:3:1. It is noteworthy that the titanium system is the only one in the presence of which it has been possible to detect the formation of the trimethylvinylsilane trimer.

The oligomerisation of trimethoxyvinyl- dimethoxymethylvinyl-, trichlorovinyl-, and dichloromethylvinyl-silanes in the presence of the system comprising tetrabutoxytitanium, triethylaluminium and triphenylphosphine has been investigated at 100–120 °C (contact time 6–10 h): [90]

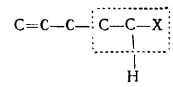


The dimerisation of methoxy-derivatives of vinylsilanes proceeds with a high selectivity. The *trans*-isomers [compounds (XXXVI) and (XXXVII)] are obtained in a yield up to 80% for a degree of conversion of the monomers of 49%. Chloro-substituted vinylsilanes dimerise less vigorously in the presence of the titanium system. Trichlorovinylsilane gives rise to a mixture of the *cis*- and *trans*-isomers (XXXVIII) and (XL) in proportions of 1:1, in 35% yield, and with a degree of conversion of the monomer of 42%. A mixture of dichloromethylvinylsilane dimers (XXXIX) and (XLI) in proportions of 1:2 is obtained in the same yield (35%).

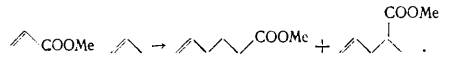
III. CO-OLIGOMERISATION OF VINYL MONOMERS WITH UNSATURATED HYDROCARBONS

1. Co-oligomerisation with Olefins

In the early stages of the investigation vinyl monomers with functional groups were subjected to a high-temperature (200–300 °C) thermal interaction with olefins. [91,92] A study was made of the behaviour of a large number of enophiles (acrylonitrile and methacrylonitrile, methyl esters of acrylic and methacrylic acids, acrylic acid, etc.) with propene, butenes, isobutene, and certain higher olefins. [91] In all cases the reaction results in the formation of adducts of the type



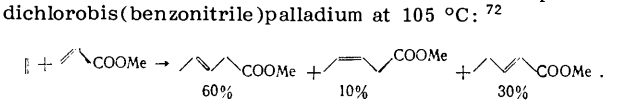
[the C–C atoms printed bold indicate the initial position of the double bond in the olefin, H is the hydrogen atom which has migrated, and C–C–X is the skeleton of the enophile with the activating functional group X (CN, COOR, etc.)]. A higher yield of adducts (up to 49%) is attained when 1,1-disubstituted ethylenes are used, for example, isobutene, while in the case of normal olefins the yield is sharply reduced (down to 18% for propene and 4% for but-2-ene). Furthermore, when normal olefins are employed, the formation of a branched adduct, whose amount increases with the number of carbon atoms in the olefin, is observed: [92]



In the codimerisation of methyl acrylate with n-hept-1-ene, the amount of the branched adduct is 25% of the total adducts.

The use of catalysts makes it possible to carry out the codimerisation under milder conditions. In the presence of ruthenium chloride, methyl acrylate reacts with an excess of ethylene at 150 °C to form a mixture of codimers (esters of pent-3-enoic acid, yield 47%) and esters of acids containing seven (12%) and nine (9%) carbon atoms. [71] A methyl acrylate dimer (yield 23%) and butene were also found among the reaction products. The same products have been obtained in the presence of rhodium chloride at 120 °C.

Three isomeric products of the codimerisation of ethylene with methyl acrylate in an overall yield of 47% relative to the methyl acrylate which has reacted are formed in the presence of dichlorobis(benzonitrile)palladium at 105 °C: [72]



An analogous mixture but with a lower yield has been obtained using the complex $[C_2H_4PdCl_2]_2$ as the catalyst. [93]

Lewis acids exert a particularly favourable effect on reactions of this kind, permitting a reduction of the reaction temperature to 25 °C and even lower. [94–99] The catalytic effect of a large number of such compounds has been studied: BF_3, BCl_3, BBr_3, $SbCl_5$, $TiCl_4$, $SnCl_4$, $AlCl_3$, and alkylaluminium chlorides ($EtAlCl_2$, Et_2AlCl, Et_3Al, $Et_3Al_2Cl_3$, Me_2AlCl, etc.). The choice of the catalyst depends on the reactivity of the enophile. Esters, including acrylates and crotonates, require stronger Lewis acids—$AlCl_3$ or $EtAlCl_2$. Aldehydes and ketones are much more reactive—in particular acrolein and crotonaldehyde react successfully with olefins in the presence of weaker Lewis acids—$ZnCl_2$ and Me_2AlCl. The use of alkylaluminium chlorides makes it

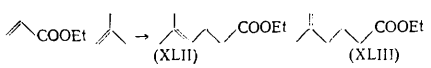
possible to avoid the proton-initiated side reactions (polymerisation of the olefin, isomerisation of the double bond in the olefin and in the co-oligomerisation products).

The results of the co-oligomerisation of vinyl monomers having functional groups with olefins depend not only on the reactivity of the enophile but also on the structure of the olefin. The following reactivity series has been found for olefins in co-oligomerisation reactions catalysed by Lewis acids: 1,1-di- > tri- > tetra- ≫ mono- > 1,2-di-substituted ethylenes.[98] As a consequence of the inadequate reactivity of long-chain olefins, for example oct-1-ene, even the presence of a strong Lewis acid ($AlCl_3$) is ineffective in the interaction of such olefins with acrylates. In such cases the addition of NaCl and KCl to $AlCl_3$ has been found to have a positive effect, permitting the formation of a codimer of methyl acrylate and oct-1-ene-, namely methyl undec-5-enoate, in 40% yield. The admixture of the unbranched ester does not exceed 4%.[96]

A satisfactory treatment of the mechanism of the co-oligomerisation reactions between vinyl monomers having functional groups and olefins in the presence of Lewis acids has not so far been achieved. According to a preliminary assessment, the interaction of the olefin with the enophile proceeds via a stage involving the formation of a complex between the enophile and the Lewis acid via a negatively charged oxygen or nitrogen atom in the enophile molecule. The activated molecule is also attacked by the other reactant in the mixture with formation of an adduct.[99]

The composition of the co-oligomerisation products formed depends not only on the structure of the initial monomers but also on the reaction conditions. In certain cases the results obtained by different workers investigating the behaviour of the same compounds under identical conditions proved to be contradictory. Thus it has been stated[100] that the co-oligomerisation of methyl acrylate with olefins in the presence of $AlCl_3$ leads to the corresponding substituted cyclobutanes. However, another investigator[95] obtained linear adducts of methyl acrylate with olefins (2-ethylbut-1-ene and methylpent-1-ene) in the presence of the same catalyst.

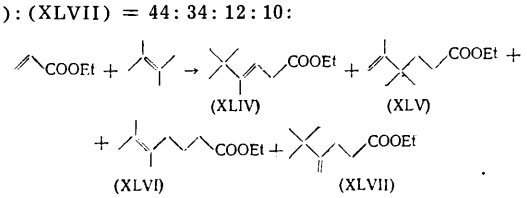
The formation of linear co-oligomers of ethyl acrylate with isobutene in the presence of $AlCl_3$ has been noted.[94] The composition of the products obtained under these conditions depends greatly on the reaction medium. The ethyl esters of 5-methylhex-4-enoic acid (XLII) and 5-methylenehexanoic acid (XLIII) are obtained in proportions of 8:1 in a mixture of dichloroethane and nitromethane:



(XLII) (XLIII)

Only the isomer (XLIII) is obtained in dry benzene.

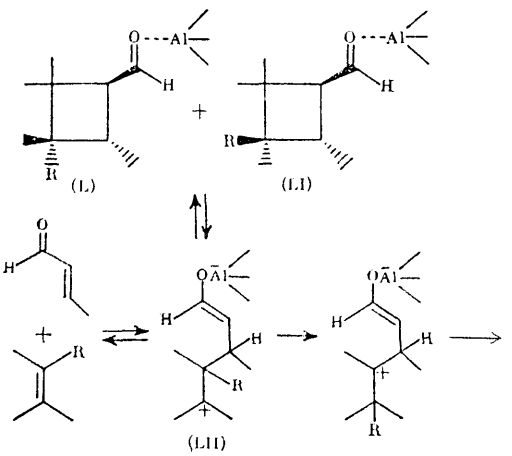
The interaction of ethyl acrylate with 2,3-dimethylbut-2-ene in a dichloroethane–nitromethane mixture led to the formation of four codimers in the proportions (XLIV):(XLV):(XLVI):(XLVII) = 44:34:12:10:

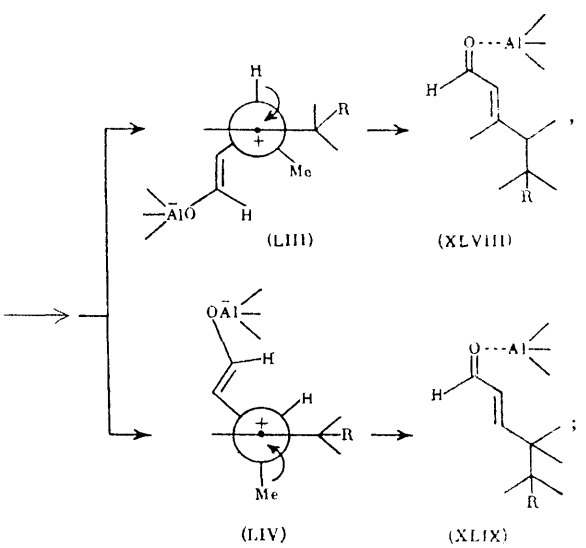


(XLIV) (XLV) (XLVI) (XLVII)

In dry benzene these monomers reacted more selectively to form compound (XLV) (only trace amounts of other isomers were found in the reaction products).

Linear and cyclic products, whose composition depends greatly on the reaction temperature, have been obtained by the reaction of αβ-unsaturated aldehydes and ketones with olefins in the presence of $EtAlCl_2$.[97] For example at 0 °C in benzene the interaction of crotonaldehyde with 2-methylbut-2-ene leads to the formation of 63% of the codimer (XLVIIIa) and 17% of the codimer (XLIXa). A mixture of 81% of cyclobutane (La), 7% of cyclobutane (Lla), 10% of the codimer (XLVIIIa), and 2% of compound (XLIXa) has been obtained at −80 °C in an overall yield of 77%. It has been suggested that the reaction proceeds via a stage involving the formation of the intermediate zwitter-ion (LIIa):

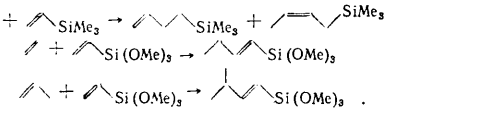




R = H (a), Me (b).

When 2-methylbut-2-ene was replaced by 2,3-dimethylbut-2-ene, the picture changed somewhat. At 25 °C the formation of only the codimer (XLIXb) in 69% yield was noted. The cyclobutane (Lb) and the codimer (XLIXb) were obtained in yields of 60% and 22% respectively in the temperature range from −80° to −40 °C. The absence of compound (XLVIIIb) is explained by the strong steric interaction between the methyl and t-butyl groups in the conformer (LIIIb).

Trimethylvinyl- and trimethoxyvinyl-silanes react with ethylene and propene in the presence of catalytic systems consisting of cobalt or titanium compounds, triphenylphosphine, and triethylaluminium in the molar proportions 1 : 1 : 4 with formation of the corresponding codimers:[101]



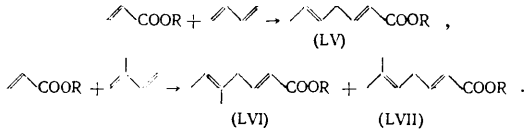
At 120 °C and for a contact time of 8–9 h the yield of the trimethylvinylsilane codimers with ethylene reaches 50% for a degree of conversion of the monomers of 65%. The codimer of trimethoxyvinylsilane and ethylene has been obtained in 36% yield for a degree of the conversion of the monomer of 80% in the presence of a catalyst containing tetrabutoxytitanium, triphenylphosphine, and triethylaluminium.

In the interaction of trimethoxysilane with propene the yield of the dimer does not exceed 28% and the degree of conversion of the monomer is 31%.

In all the reactions described, 10–25% of the products of the linear dimerisation of vinylsilanes were formed together with the codimers; the dimerisation of α-olefins has not been observed.

2. Co-oligomerisation of the Alkyl Esters of αβ-Unsaturated Carboxylic Acids with Dienes, and Trienes

The co-oligomerisation with dienes has been investigated in fair detail. In the early studies devoted to the co-oligomerisation of alkyl acrylates with buta-1,3-diene and isoprene the corresponding linear dienes were obtained and the structures of the alkyl esters of hepta-4,6-dienoic and 6-methylhepta-4,6-dienoic acids respectively were attributed to them.[102–104] However, it was subsequently shown that the alkyl esters of hepta-2,5-dienoic acid (LV) or 5-methylhepta-2,5-dienoic acid (LVI) and 6-methylhepta-2,5-dienoic acid (LVII) are formed:[105]



When cobalt acetylacetonate and triethylaluminium are used as the catalytic system, the yield of the co-oligomers of butadiene with alkyl acrylates is 20–30% and in the case of isoprene it amounts to 35–45%. The esters of hepta-3,5-dienoic acid (2–3%) and oligomers with a high molecular weight have been detected in the reaction products.

Conditions have been found for the codimerisation of isoprene with methyl acrylate whereby it is possible to obtain a mixture of *cis*- and *trans*-6-methylhepta-2,5-dienoic acids in 70–80% yield relative to the methyl acrylate which has reacted for a degree of conversion of isoprene of 70–80% and of methyl acrylate of 90–95% in the presence of catalytic systems incorporating cobalt(II) acetylacetonate, and organoaluminium reductant, and an electron-donating modifying agent.[106] Apart from triethylaluminium, which is most widely employed, tris(3-methylhepta-4,6-dienyl)aluminium and tris(cyclohexenylethyl)aluminium have been used, as reductants, because they do not ignite on contact with air and water and ensure a higher yield of co-oligomers. Triphenylphosphine, triphenylstibine, and triphenoxystibine proved to be the best modifying agents. The ratio of the *cis*- and *trans*-isomers (~2 : 1) is independent of the catalyst and the reaction conditions. Small amounts (2–5%) of a cyclic adduct, the methyl ester of cyclohex-3-ene-1-carboxylic acid, were found in the reaction products. The content of higher oligomers did not exceed 2–5%.

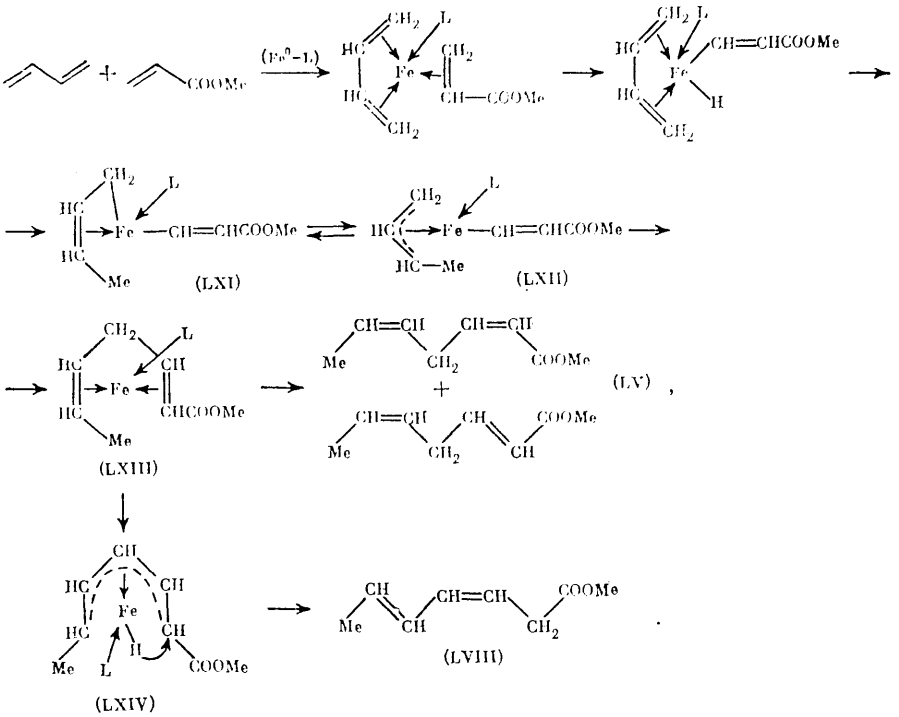
The behaviour of 1,3-dienes and alkyl acrylates in the presence of iron-containing complex catalysts has been studied in very great detail.[107–113] As a result of the co-oligomerisation of buta-1,3-diene with methyl acrylate in the presence of systems comprising iron acetylacetonate and trialkylaluminium, a mixture of the methyl esters of hepta-2,5-dienoic acid and hepta-3,5-dienoic acid (LVIII) is formed with the former predominating (80–87%), compound (LVIII) being produced as a result of the isomerisation of the ester (LV), which could be prevented in certain cases.[107,108] In addition, insignificant amounts of the methyl esters of hepta-4,6-dienoic acid and cyclohex-3-ene-1-carboxylic acid (LIX) have been found. The overall yield of codimers does not exceed 34–35% relative to the initial methyl acrylate. The optimum temperature range is 60–90 °C, since at lower temperatures the degree of conversion of the initial monomers is insignificant, while at higher temperatures cyclodimerisation begins to predominate. The ratio of the initial reactants has little influence on the yield of the required products, while the ratio Al : Fe has a significant effect on the process selectivity. The addition of powerful electron-donating compounds, namely amines, phosphines, and phosphites, which increase the activity of the catalyst, has a considerable effect. As a rule, the presence of these ligands in the reaction medium promotes the formation of the cyclic dimer. The best yields of linear codimers have been obtained using triphenylstibine Ph_3Sb and triphenyl antimonite $(PhO)_3Sb$.[109]

The degree of conversion can be altered and the codimerisation can be directed towards the formation of a particular product also with the aid of solvents. In solution in benzene the degree of conversion of the monomers reaches 95–100%, but most of them are converted into higher oligomers and the yield of codimers varies in the range 10–50% depending on the modifying agent. The selectivity of the codimerisation carried out using ethers as solvent is very high. In this case the yield of the geometrical isomers of the methyl esters of hepta-2,5-dienoic acid reaches 100% relative to the methyl acrylate which has reacted, but the degree of conversion of the monomers falls to 45–55%.[109] The combination of methylene chloride (solvent) with pyridine (electron donor) makes it possible to obtain the virtually pure (93.6%) cyclic codimer (LIX).

The authors explain the high selectivity of the reaction in ethers, particularly in tetrahydrofuran, by the fact that the ether, which is an active two-electron ligand, creates steric hindrance to the approach of the codimer molecules to the metal, while the sterically less hindered monomer molecules are coordinated without special difficulty.

The influence of the addition of copper, cobalt, nickel, manganese, and lanthanide (La, Ce, Eu, Tb, Dy, and Sm) acetylacetonates on the activity and selectivity of the catalytic system $Fe(acac)_3$–$SbPh_3$–$AlEt_3$ has been investigated.[110] With the exception of $Sm(acac)_3$, which increases the yield of the co-oligomerisation products by 12.5%, the derivatives of the other elements not only had a negative effect on the yield of the co-oligomers but also promoted the appearance, together with the esters of hepta-2,5-dienoic acid, of the ester of the conjugated hepta-3,5-dienoic acid and the cyclic adduct (LIX). Depending on the nature of the added metal and its amount, it is possible to obtain the conjugated ester or the cyclic adduct in a virtually pure form (98.5–100%), but in a low yield.

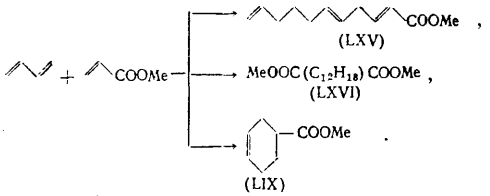
Experiments with deuterated monomers suggested the following mechanism of the codimerisation reaction:[107,111,112]



The interaction of butadiene with methyl acrylate includes the stage involving the oxidative addition of methyl acrylate to the iron atom, which leads to the hydride complex (LX), within which a proton is transferred to the activated butadiene molecule; isomerisation results in the formation of the σ,π-allyl complex (LXII). The subsequent dimerisation of the coordinated ligands leads to the formation of a new intermediate complex (LXIII); in the presence of an excess of the monomers the latter decomposes with formation of the stereoisomeric methyl esters of hepta-2,5-dienoic acid and the initial complex. In benzene (instead of tetrahydrofuran) solution the final reaction product is the isomer (LVIII) with conjugated double bonds, whose formation proceeds via the hydride complex (LXIV). The low process selectivity in the formation of codimers in benzene solution can be accounted for by the involvement of the resulting conjugated ester in subsequent reactions, leading to higher oligomers.

The co-oligomerisation of acrylic and methacrylic acids with an excess of 1,3-dienes in the presence of zerovalent nickel complexes leads to other products, formed from two and more molecules of the initial monomers. The catalyst is prepared by reducing nickel acetylacetonate (or other nickel salts) with an organoaluminium reductant in the presence of butadiene and an electron-donating organophosphorus modifying agent (phosphine or phosphite) with the addition of an inert diluent—benzene, toluene or other hydrocarbons.[114,115]

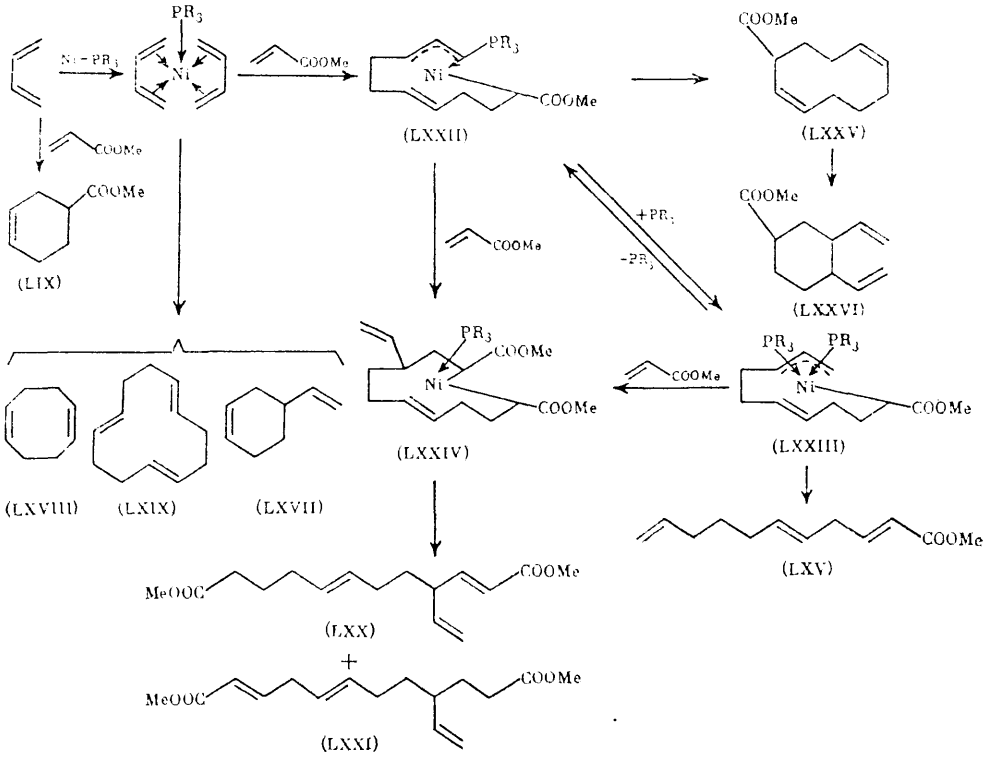
The available data on the composition of the co-oligomerisation products are contradictory. Thus it has been stated[115] that the co-oligomerisation of methyl acrylate with buta-1,3-diene at 120–165 °C leads to the formation of the methyl esters of undeca-2,5,10-trienoic acid (LXV) and cyclohex-3-ene-1-carboxylic acid (LIX), as well as the dimethyl ester of dodecatrienedicarboxylic acid (LXVI) in yields of 40.3, 8.2, and 46.5% respectively:



Other workers[116,117] obtained under the same conditions a mixture containing methyl undeca-2,5,10-trienate (LXV), 4-vinylcyclohexene (LXVII), cyclo-octa-1,5-diene (LXVIII), *trans, trans, trans*-cyclododeca-1,5,9-triene (LXIX), methyl cyclohex-3-ene-1-carboxylate (LIX), methyl 4-vinyldodeca-2,7-dienedioate (LXX) and methyl 4-vinyldodeca-7,10-dienedioate (LXXI). The yield of compound (LXV) varies in the range 15–25%.

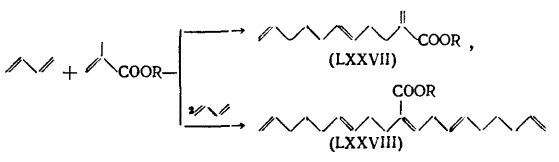
Extensive studies have been made on the influence of the structure of electron-donating modifying agents, organoaluminium reductants, and solvents on the yield and composition of the products of the co-oligomerisation of methyl acrylate with butadiene.[116] The highest yield of the ester of undeca-2,5,10-trienoic acid(LXV) (75%) has been obtained in the presence of a catalyst consisting of nickel acetylacetonate, triphenylphosphine, and tris(3-methyl-hepta-4,6-dienyl)aluminium in proportions of 1 : 2 : 4. Triphenyl phosphite and tris(β-ethoxyethyl) phosphite drive the reaction towards the formation of compounds (LXX) and (LXXI), whose contents in the reaction products reach 87 and 83% respectively for an overall yield of the co-oligomers of 96%.[117] The temperature range 120–160 °C is optimal for the synthesis of compound (LXV); the maximum yields of the esters of vinyldocadienedioic acids are obtained in the range 40–80 °C depending on the structure of the activator. The most suitable solvents are toluene, benzene, and hexafluorobenzene.

The authors proposed the following co-oligomerisation mechanism:[116,117]



In the first stage butadiene and methyl acrylate are coordinated to the zerovalent nickel atom and form a coordination-unsaturated nickel σ,π-complex (LXXII) which can give rise to two 18-electron complexes (LXXIII) and (LXXIV) depending on the temperature. At an elevated temperature the complex (LXXIII), which gives rise to the ester of undeca-2,5,10-trienoic acid (LXV), is more stable. The insertion of methyl acrylate in the π-allyl–Ni bond at a lower temperature leads to the irreversible conversion of the complex (LXXIII) into the σ,σ-complex (LXXIV), which is transformed into the isomeric esters of vinyldodecadienedioic acids (LXX) and (LXXI). The formation of methyl 3,4-divinylcyclohexane-1-carboxylate (LXXVI) can be represented as a process proceeding via a stage involving the formation of the cyclic co-oligomer (LXXV) with its subsequent Cope rearrangement to the ester (LXXVI).

Numerous studies of the influence of various factors on the co-oligomerisation of buta-1,3-diene with methacrylic acid esters in the presence of nickel catalysts showed that three main products are formed: alkyl undeca-1,5,10-triene-2-carboxylate (LXXVII) and two isomeric alkyl esters of nonadeca-1,6,9,13,18-pentaene-10-carboxylic acid (XXVIII):[118]



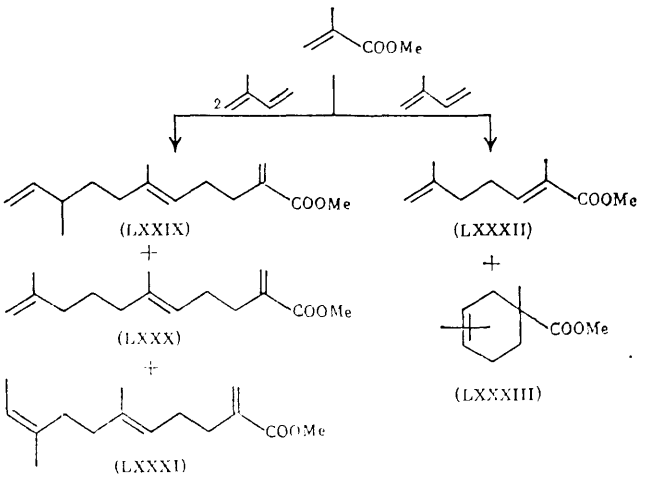
At 50 °C in the presence of a catalytic system comprising nickel acetylacetonate and triethylaluminium without activator, the yield of compound (LXXVII) reaches 24% and that of compound (LXXVIII) 54%. An increase of temperature promotes the formation of butadiene cyclisation products: cyclo-octa-1,5-diene and cyclododeca-1,5,9-triene.

One cannot say that all the data obtained reflect very clearly the influence of the structure of electron-donating ligands on the course of the co-oligomerisation of butadiene with alkyl methacrylates and the authors' conclusions can therefore be adopted only with some reservations. They believe that phosphines inhibit co-oligomerisation. Phosphites, particularly tris(o-biphenylyl) phosphite, promote the formation of cyclo-octa-1,5-diene (yield up to 60%). Phosphorous acid trimorpholide promotes the formation of compound (LXXVIII) in a good yield (69% after 120 h at 20 °C). In the presence of triphenylphosphines the above co-oligomer was isolated in a yield of 62% under analogous conditions. An appreciable yield of compound (LXXVIII) (79–87%) has been obtained in the presence of triphenylstibine. Like triphenylarsine, this ligand is more reactive and selective than triphenylphosphine (in the presence of triphenylarsine it was possible to achieve a 93% yield of methyl nonadeca-1,6,9,13,18-pentaene-10-carboxylate). Very high yields of compound (LXXVIII) (up to 88–92%) have been obtained using pyridine as the ligand. Its methyl, methoxy- and chloro-derivatives are less reactive.

The influence of the nature of nickel compounds on the results of the co-oligomerisation of buta-1,3-diene with methacrylates has been investigated.[118] In the presence of catalytic systems containing chloride ions co-oligomerisation does not occur. Satisfactory results have been obtained when nickel acetylacetonate was replaced by benzene-soluble nickel salts of lauric, palmitic, and certain other organic acids.

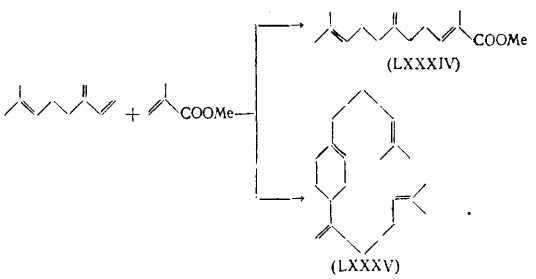
The co-oligomerisation of methyl methacrylate with isoprene and myrcene has been investigated in the presence of a homogeneous nickel catalyst (nickel acetylacetonate, reductant—ethoxydiethylaluminium).[119] The reaction with isoprene in the presence of this catalyst gives rise to three

main products: the methyl esters *trans*-6,9- and *trans*-6,10-dimethyl-2-methyleneundeca-5,10-dienoic acids (LXXIX) and (LXXX) and methyl *trans*, *cis*-6,9-dimethyl-2-methyleneundeca-5,9-dienoate (LXXXI) in proportions of 4 : 1 : 2 in an overall yield of 61% relative to the isoprene which has reacted.[119] Methyl *trans*-2,6-dimethylhepta-2,6-dienoate (LXXXII) and a cyclic adduct of isoprene and methyl methacrylate (LXXXIII) in an amount of 3% have also been found in the reaction products.



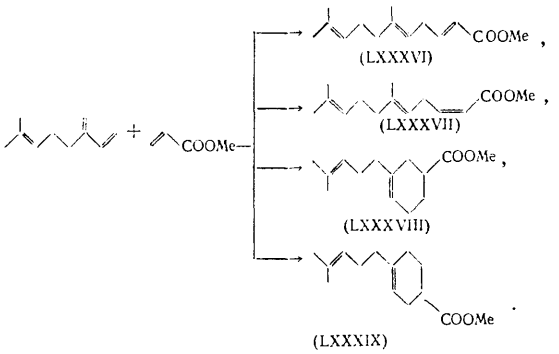
The co-oligomerisation was carried out at 66–76 °C for 8 h in toluene The degrees of conversion of isoprene and methyl methacrylate were 36 and 18% respectively. There was a considerable proportion (27.6%) of high-boiling products (residue after distillation).

Myrcene reacts with methyl methacrylate in the presence of nickel catalysts much more readily than isoprene. After only 1 h at 100 °C, the degree of its conversion reaches 95%, while that of methyl methacrylate reaches 20%. The main reaction products are methyl *trans*-2,10-dimethyl-6-methyleneundeca-2,9-dienoate (LXXXIV) (11.2%) and camphorene (LXXXV) (35.2%):



The co-oligomer of myrcene and methyl methacrylate with a molecular weight of 372 (27.6%) and high-boiling fractions of unknown composition (~23%) are formed as by-products.[119]

The codimerisation of myrcene with methyl acrylate has been been investigated in the presence of iron and cobalt complexes. It leads to the formation of linear codimers—methyl 6,10-dimethylundeca-2-*cis*(*trans*), 5-*trans*, 9-trienoates (LXXXVI) and (LXXXVII) and cyclic diene synthesis products (LXXXVIII) and (LXXXIX):[120]



Apart from these compounds, up to 8–10% of unidentified higher oligomers are formed in the reaction. The yields and proportions of the linear and cyclic codimers depend on the composition of the catalyst and the reaction conditions.

The maximum yield of the co-oligomerisation products is 75–80% relative to the myrcene which has reacted (the unreacted monomer is fully returned to the reactor); the degree of conversion of myrcene is up to 60–68%. The highest yield of linear codimers has been obtained in the presence of the catalytic system comprising $Fe(acac)_3$, PPh_3, and $AlEt_3$ in tetrahydrofuran. Cyclic esters are formed in this case in an amount of 17% of the total yield of the codimer. The content of cyclic products increases to 36–43% when $SbPh_3$, $P(C_6H_{11})_3$, and $Sb(OPh)_3$ are used as modifying agents. Cobalt compounds direct the reaction towards the formation of cyclic esters. Thus the addition of only 1% of cobalt acetylacetonate to the above catalytic system increases the yield of cyclic codimers to 50%. The complete replacement of iron acetylacetonate by cobalt acetylacetonate makes it possible to obtain the almost pure cyclic ester (LXXXVIII).

The solvents have an appreciable influence on the course of the reaction. On passing from ester solvents to aromatic hydrocarbons, the overall yield of codimers falls, but the fraction of cyclocodimerisation products and higher oligomers increases. A temperature of 50 °C is optimal; when it is reduced to 25 °C, the necessary reaction time increases sharply (from 10 to 100 h) and the yield of the codimers also remains low under these conditions.

The methyl esters of *cis*, *trans*, *trans*- and *trans*, *trans*, *trans*-undeca-2,5,9-trienoic acids in an overall yield up to 80% have been obtained on co-oligomerisation of methyl acrylate with octa-1,3,6-triene in the presence of systems consisting of iron or cobalt acetylacetonate, a phosphine modifying agent, and triethylaluminium.[121]

The possibility of the electrochemical cross-hydrodimerisation of 1,3-dienes, in particular butadiene, with ethyl acrylate and crotonate has been described.[122] The reaction proceeds via the recombination of intermediate radical-anions formed on the surface of the cathode at −15° or −20 °C. Dimethylformamide (DMF), anhydrous or containing 10% of water, or a 2:1 mixture of hexamethylphosphoramide and isopropyl alcohol with added tetrabutylammonium iodide, which increases the electrical conductivity of the electrolyte, have been used as solvents.

The composition and yield of the reaction products depend on the composition of the electrolyte. Thus in anhydrous DMF ethyl acrylate reacts with butadiene to form 1% of ethyl *trans*-hept-5-enoate (the product of the codimerisation of one molecule of buta-1,3-diene with one molecule of ethyl acrylate), 2.5% of diethyl *trans*-dec-5-enedioate (the product of the codimerisation of one molecule of buta-1,3-diene with two molecules of ethyl acrylate), and 7.5% of diethyl adipate

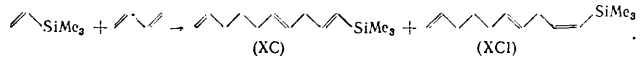
(the ethyl acrylate hydrodimerisation product). In aqueous DMF the yield of the ester of *trans*-dec-5-enedioic acid increases to 6.5%, that of diethyl adipate rises to 60%, while the ester of *trans*-hept-5-enoic acid was not detected in the reaction products.

Ethyl crotonate reacts with buta-1,3-diene in anhydrous DMF to form 8.7% of ethyl *trans*-3-methylhept-5-enoate and 5% of diethyl 3,4-dimethyladipate. In a mixture of the amide and the alcohol the yield of the 3,4-dimethyladipic ester increases to 68.7% and 7.9% of diethyl *trans*-3,8-dimethyldec-5-enedioate is formed instead of 3-methylhept-5-enoic acid ester.

3. Co-oligomerisation of Vinyl Derivatives of Silicon with Dienes and Trienes

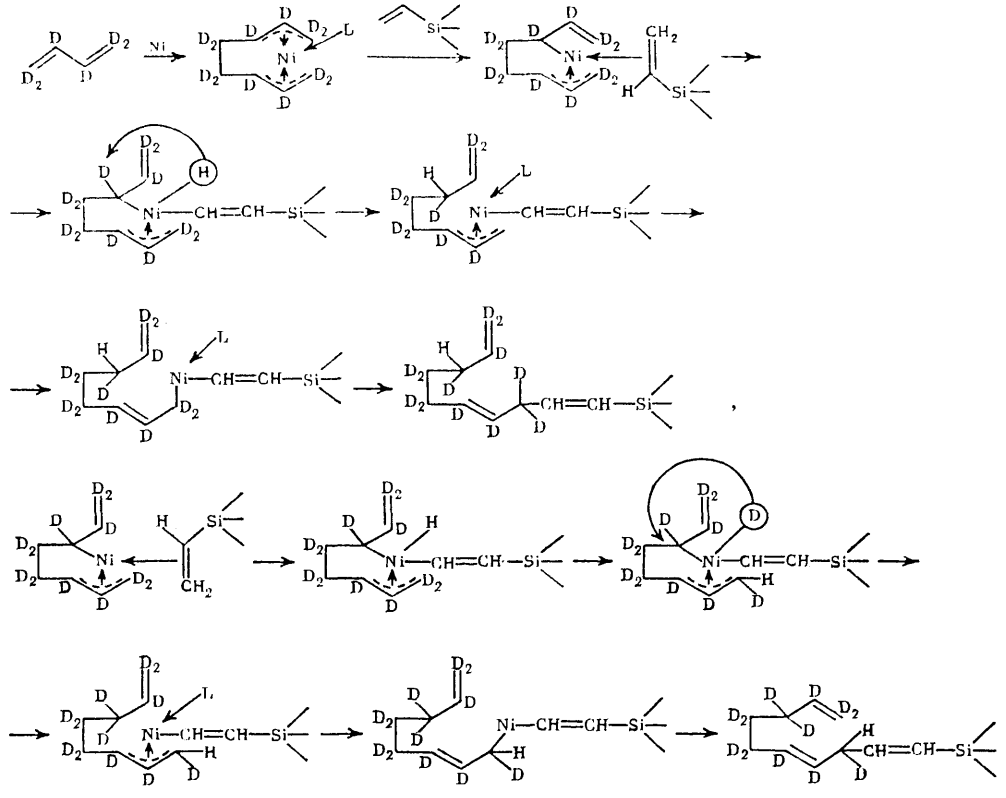
The linear co-oligomerisation of vinylsilanes with dienes and trienes is a new convenient procedure for the preparation of silicon-containing polyenes, which can serve as starting materials for the synthesis of a whole series of valuable products. These reactions have become the subject of study comparatively recently but extensive experimental data have already accumulated. These confirm that reactions of this kind can be carried out effectively.

The co-oligomerisation of butadiene with trimethylvinyl- and trimethoxyvinyl-silanes in the presence of the catalytic system consisting of nickel acetylacetonate, triphenylphosphine, and triethylaluminium has been investigated.[123–125] The co-oligomerisation with trimethylvinylsilane (100 °C, 8–10 h) results in a mixture of the silyldecatrienes (XC) and (XCI) in proportions of 1:1, which is obtained in a yield of 72%:

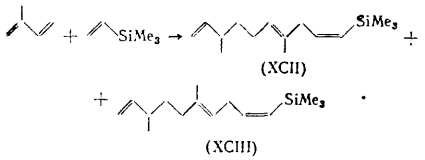


(XC) (XCI)

A change in the ratio of the initial monomers does not affect the composition of the reaction products. The formation of cyclic co-oligomers and homo-oligomers of the initial reactants has not been detected. Under analogous conditions, trimethoxyvinylsilane reacts with butadiene to form only one product—*cis*, *trans*-1-trimethoxysilyldeca-1,4,9-triene. The interaction of trimethylvinylsilane with deuterated butadiene has been studied and this has led to the following reaction mechanism:



Under the conditions described above, isoprene and trimethylvinylsilane react to form a mixture of isomeric silylated trienes (XCII) and (XCIII) in proportions of 3:1 and in a yield of 82%: [125]



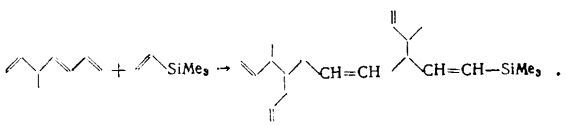
(XCII)

(XCIII)

Trimethoxyvinylsilane reacts with isoprene more selectively, giving rise to a 75% yield of pure *cis*, *trans*-1-trimethoxysilyl-5,8-dimethyldeca-1,4,9-triene. The only product of the co-oligomerisation of trimethylvinylsilane with piperylene is *trans*, *trans*-1-trimethylsilyl-3,7-dimethyldeca-1,4,9-triene (yield 70%):



Trimethylvinylsilane is more inert in the reaction with 3-methylhepta-1,4,6-triene. The yield of a mixture of the geometrical isomers of 1-trimethylsilyl-3-(1′-but-3′-enyl)-7-(1′-prop-3′-enyl)-8-methyldeca-1,4,9-trienes was only 30%:



The interaction of butadiene with trimethylvinylsilane in the presence of the catalytic system comprising nickel chloride, triphenylphosphine, and ethylaluminium sesquichloride($AlEt_{1.5}Cl_{1.5}$) is of the type of a telomerisation reaction and is completed by the formation of telomers having the general formula $H(CH_2CH{=}CHCH_2)_nC(=CH_2)SiMe_3$, where $n = 1-5$.

After 5 h at 60 °C, a mixture of hexadienyl- and decatrienyl- silanes is formed in an overall yield of 97% and with a degree of conversion of trimethylvinylsilane of 42%. [126] On increasing the temperature to 100 °C and the reaction time to 8 h, tetradecatetraenyl- and octadecapentaenyl-silanes are formed together with hexadienyl- and decatrienyl-silanes in an overall yield of 73% and with a degree of conversion of trimethylvinylsilane of 85%. Homo-oligomers of butadiene were not detected in the reaction products.

The co-oligomerisation of dichloromethylvinylsilane with butadiene in the presence of a catalyst consisting of tetrabutoxytitanium, triphenylphosphine, and triethylaluminium proceeds with formation of a mixture of *trans*, *trans*-hexa-1,4-dienyl- and *trans*, *trans*, *trans*-deca-1,4(5),8-trienyldichloromethylsilanes in proportions of 2:3. [127] The co-oligomerisation of butadiene with dimethoxymethylvinylsilane has been carried out successfully in the presence of the same titanium catalytic system, but in this case the formation of a mixture of decatrienylsilane isomers was established. [127] The use of nickel chloride, triphenylphosphine, and ethylaluminium sesquichloride made it possible to improve the selectivity of the reaction and to obtain the pure cotrimer—*trans*, *trans*-deca-1,4,9-trienyldimethoxymethylsilane. [127]

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Analysis of the data presented shows that catalytic systems permitting the oligomerisation reactions of olefins containing powerful electron-donating or electron-accepting substituents in direct proximity to the double bond have already been investigated. These processes resemble the oligomerisation reactions of olefins without functional groups which have been thoroughly studied. Further successful search for effective catalytic systems should therefore be directed towards the selection of the appropriate ligand environment around variable-valence metals, which will make it possible to achieve the required mode of oligomerisation of vinyl monomers ensuring the introduction into the final product of the necessary number of the functional groups present in the initial monomer. The highly effective electrochemical oligomerisation reactions of substituted olefins also merit the most careful attention.

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All-Union Research and Design
Monomer Institute, Tula

Translated from *Uspekhi Khimii*, 53, 1380-1406 (1984)

Structure and Properties of Block Copolymers of Polystyrene and Polybutadiene

A.A.Askadskii, T.A.Andryushchenko, and P.I.Zubov

Recent studies of the structure and properties of block copolymers of polystyrene and polybutadiene are reviewed, with special emphasis on the effect of the structure and of the formation conditions for the samples on the interrelated physico-mechanical properties. Problems associated with the macro- and micro-layering of block copolymer solutions are examined in detail. Work on the analysis of block copolymer structures from measurements of sorption characteristics is reviewed in the light of an assumed relaxation mechanism for the sorption and swelling processes. The prospects of controlling the structure and properties of block copolymers are shown to be good.
The bibliography contains 190 references.

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I. INTRODUCTION

The literature on the structure and properties of block copolymers is now extensive. Some recent reviews[1-4] include work on the structure and properties of block copolymers published up to 1976: they deal mainly with thermoelastoplastics, i.e. systems in which fairly large flexible blocks of elastomers are chemically bound to equally large rigid blocks.

Thermoelastoplastics in the form of block copolymers are thought to be promising materials with a wide range of prospective applications in technology.[5] They are simple to prepare and not very different from ordinary plastics in the fabrication of components. The addition of block copolymers (for example, polystyrene/polybutadiene) of the styrene–butadiene–styrene type (SBS) to ordinary plastics polyethylene, polypropylene, polystyrene) improves their elasticity and raises their impact resistance. Yet the workability of the compositions remains almost the same as that of the initial plastics. The potential applications of block copolymers stem from the overall effect of these properties. The most substantial developments have been achieved for block copolymers of polystyrene and polybutadiene, and the present review will deal mainly with these systems.

Block copolymers (especially those based on polystyrene) have attracted sustained development because their practical applications are already considerable.[6-11] The rheological properties of block copolymers are complex, and they differ from those of the dispersed system and of homopolymers. These problems are specially reviewed in Ref. 12. Other review articles[13-16] discuss the morphology of block copolymers, their mechanical properties, and the dependence of their properties on composition and on the measurement conditions.

This review will examine in detail only the most recent results, published in the last few years, though reference to earlier work will be made, where necessary, to make the presentation more logical. No attempt will be made to deal with the historical aspects of the problem.

II. CONFORMATIONAL STATE OF MACROMOLECULES IN SOLUTIONS. EFFECT OF THE COMPOSITION OF THE SOLVENT MIXTURE. MICRO- AND MACRO-LAYERING OF BLOCK COPOLYMER SOLUTIONS

As was stated above, block copolymers consist of large fragments of one polymer chemically bound to fragments of another polymer. In the case of block copolymers of polystyrene and polybutadiene the central block is a fragment of a polybutadiene chain, and the two end blocks are polystyrene (this is the commonest structure, though other variants are possible).

The behaviour of block copolymers in solution was studied even in earlier work. The characteristic form of block copolymers produces specific structures even in dilute solutions, though some workers believe that theories developed for homopolymers[17-19] can be applied to block copolymers. It has been shown fairly convincingly that intramolecular phase separation often takes place in dilute solutions. As a result, micelles are formed, consisting of the block whose thermodynamic affinity for the solvent is lower, with a shell of the block whose thermodynamic affinity for the solvent is higher.[20-22] By varying the composition of the surrounding medium we can control the segregation of the blocks, as has been predicted theoretically.[23-25] The structure of the micelles can be varied by adding a selective precipitant, and this method has been used widely to control the properties of the resulting samples.[26-32] The introduction of a selective precipitant into a block copolymer solution causes coiling of one of the blocks and hence lowers the characteristic viscosity of the solution.[33-36]

Micro-layering in solutions of block copolymers and the mutual compatibility of the two blocks depend on the type of solvent, and on whether the solvent is a common solvent for both blocks or a selective solvent for one of them.[37] In the determination of the phase state of block copolymers in solution the most important consideration is the intermolecular interaction between the blocks and their interaction with the solvent. A change from dilute to concentrated solutions is not always possible: specific conditions

may be necessary. Thus for an equimolar ratio of the components in a copolymer of the ABA type this change is possible only in solvents selective towards the central block;[38] in other solvents phase separation takes place, with precipitation of the polymer.

Depending on the character of the intermolecular interaction between the like and the unlike blocks, the chains of block copolymers may take on different shapes.[39] Thus if the AA and BB interactions are negligible, and the AB interaction results in attraction between the segments, the chains are coiled into a tight ball. On the other hand in the case of mutual attraction between like blocks and mutual repulsion between unlike blocks we observe a collapse of the chains of a three-block copolymer.

Of course, the type of structure formation in block copolymers in solution depends not only on the concentration but also on the type of the solvent. If we use a solvent which is thermodynamically poor for the polybutadiene blocks (for example, ethyl acetate) the ternary block copolymer of polybutadiene and polystyrene in solution forms spherical or worm-like micelles whose core consists of polybutadiene blocks.[40]

As was mentioned above, in selective solvents the block copolymers form micelles consisting of a dense core (contributed by the less soluble component) and a shell, containing the more soluble component and therefore swelled by the solvent. The tendency of block copolymers to form micelles depends on their composition, on the molecular weight of the blocks, and on other factors. For block copolymers of polystyrene with polybutadiene the micelle formation process is conveniently studied in n-alkane solutions. A study[41] by light scattering and sedimentation methods has shown that depending on the molecular weight of the blocks, on the type of solvent, on the concentration of the polymer in solution, and on the temperature, the system can exist as a homogeneous solution and as a micellar structure, with possible transitions between the two states. The molecular weight of the polystyrene has the dominant effect on the type of structure formation in the solutions. If these blocks have a relatively small molecular weight (less than 10000) true solutions are formed in n-alkanes, but if their molecular weight is greater than 20000 only micellar solutions are formed. We note that the number of molecules in the micelle depends on the method of preparing the solution and on the molecular weight of the polystyrene blocks. Micelle formation in solutions of block copolymers of polystyrene and polybutadiene in selective solvents is discussed also in Ref. 42.

In work with solutions of block copolymers (in particular, ternary block copolymers of polystyrene and polybutadiene) it is important to allow for the special behaviour and for the instability of these substances. Thus an anomalous opalescence has been observed in solutions of this block copolymer in isopropyl acetate,[43] which is a selective solvent for polystyrene. The anomaly occurs in a narrow temperature range (37–35 °C): it is due to a change in light scattering caused by the formation of large particles under these conditions. The opalescence temperature decreases as the concentration of the solution is decreased, and micelles of normal size are formed. The formation of anomalously large micelles is an unstable process which can be observed over periods of several hours.

A metastable state was observed[44] in a detailed study of the viscosity of binary block copolymer solutions (polystyrene and polybutadiene) in solvents selective for the individual blocks as well as in mixtures of these solvents. Transitions from one type of micelle to the other were observed after changing the composition of the mixture (by gradually changing from a solvent selective for one of the blocks to a solvent selective for the other); the transition occurs through a region of metastability. This transition is accompanied by characteristic changes in the viscosity of the solution and in the selective sorption coefficient for one of the components of the mixture. All these properties depend on the molecular weight of the blocks of polystyrene and polybutadiene.

The association of block copolymers in selective solvents has been studied[45] with hydrogenated block copolymers of polystyrene and isoprene. At high concentrations of the selective solvent and low temperatures, compact monodispersed micelles were formed. At lower concentrations of the selective solvent and higher temperatures, the associations were larger and polydispersed.

The conformational state of block copolymers in dilute solutions has been analysed in a computer experiment,[46] applying the Monte Carlo method to a simple cubic lattice in which self-intersections were forbidden. The most significant conclusion[46] was that in ternary block copolymers the middle block has a higher swelling coefficient than in a homopolymer of the same structure. Furthermore the ternary block copolymer is larger than the equivalent binary block copolymer. These results were confirmed by experimental measurements of viscosity and light scattering in the same investigation.[46]

Various methods have been used to study micro-layering in solutions of block copolymers. One of these consists in determining the solubility parameters of the blocks of the copolymer and of the solvent.[47] This approach in many cases allows qualitative predictions of the phase state of the block copolymer–solvent system as a function of the chemical structure of the blocks and of the solvent molecules. An alternative approach relies on a theoretical analysis of the thermodynamics of the micelle formation processes and of phase separation in dilute solutions of block copolymers.[48]

The compatibility of the blocks in block copolymers may differ from that of the corresponding homopolymers. This effect is observed[49] in thermodynamic studies, for example in calculations of the free energy of mixing of the components. It is found that the homopolymers are less easily integrated than blocks of the same structure incorporated in a block copolymer.

Many workers have analysed the micro-layering effect theoretically and tested their results experimentally. The theory proposed by Leary and Williams[50] was further developed by Pico and Williams:[51] it relates to systems in which the polymer is predominant and the solvent is present only in small amounts. It is shown that even if the solvent is good for both blocks the system can undergo micro-phase separation at high enough concentrations, as in the case of cooled melts. By assigning a geometrical shape to the domains consisting of blocks of either component the Gibbs free energy could be calculated. A comparison of these results with those for a random mixture of the components allowed the layering temperature of the system and its dependence on the volume fraction of the solvent to be determined. The lowest layering temperature is obtained when the solubility parameter of the solvent is equal to the half-sum of the solubility parameters of the blocks of which the copolymer is composed.

The proposed model was tested experimentally by light transmission and by rheological methods.[52] Plasticised samples of the block copolymer were used in light transmission measurements, and the frequency dependence of the dynamic viscosity of the same samples was measured over a wide temperature range. Dipentane (a good solvent for both types of block) was used as the plasticiser/solvent. At the layering temperature of the micro-blocks all the measured

characteristics show a sudden change, and therefore this temperature can be measured very accurately. The agreement between experiment and theory was good except when the micro-layering temperature was lower than the glass transition temperature of the polystyrene blocks.

Many studies of the rheological properties of block copolymer solutions have been reported.[53-55] If the chosen solvent is a good solvent for both blocks the rheological behaviour of the solution is the same as that of a homopolymer solution. In the presence of selective solvents, in which the solubility of one of the blocks is temperature-dependent, very different properties are observed.[53]

Similar results were reported from a study[54] of the rheological behaviour of concentrated solutions of block copolymers of polystyrene and polybutadiene, having a four-pointed star structure. When a solvent common to both blocks was used the rheological behaviour of the solutions was indistinguishable from that of homopolymer solutions. When the solvent was selective for one of the blocks the rheological results were difficult to reconcile with conventional views.

The work was later extended[55] to other solvents and other methods of studying rheological properties. The rheological behaviour of block copolymers in solutions can be explained by postulating a macroscopic network formed by the polystyrene domains in the solution. This network is unstable and can be broken down by mechanical stresses.[56] Intermolecular interaction, depending on the type of solvent and on its selectivity towards the blocks, can play a major role in these effects.

As was pointed out above, the type of structure of a block copolymer in solution depends on the concentration. The appearance of viscoelastic properties in these systems suggests[57] the formation of a continuous lamellar structure (arising from the polystyrene domains) at high concentrations. Below some limiting concentration the solution develops a network whose points consist of polystyrene domains. The solution becomes truly molecular only at high dilutions.

There are also reports[58] that block copolymers in solutin can exist in a mesomorphic state at high concentrations.

Various papers discuss the compatibility of block copolymers in solution with homopolymers having the same structure as one of the blocks. Thus the compatibility of polystyrene/polybutadiene block copolymers with a butadiene homopolymer in solution was determined viscometrically, and compared with the compatibility of polybutadiene with the random copolymer.[59] The latter was found to be more compatible with polybutadiene, the compatibility decreasing as the molecular weight of the block copolymer increases.

The second virial coefficient for block copolymers of polystyrene and polybutadiene and for mixtures of polystyrene and polybutadiene of the same composition was determined (in different solvents) by an osmometric method.[60] A difference between the second virial coefficients was detected for these systems, but the difference was decreased by raising the temperature and by increasing the proportion of polystyrene in the mixture. Structure formation by the block copolymers in solution was studied using the polarised luminescence method, and it was shown that globular, dumb-bell, and other structures can develop, depending on the type of solvent.[61]

Brief mention should be made of the special features of the fractionation of block copolymers. Fractionation methods applicable to block copolymers, including gel chromatography, precipitation chromatography, and fractional precipitation are discussed in Ref. 62. Compositional non-uniformity in block copolymers has been successfully analysed by gel-permeation chromatography.[63] The study of the molecular weight of block copolymers by gel chromatography is complicated by the special structure of these materials, which causes difficulties in the choice of solvent. A detailed discussion of these problems will be found in Ref. 64. The specific problems of the chromatographic separation of block copolymers on porous adsorbents are discussed in Ref. 65. The separation theory developed in that work[65] can identify the most favourable conditions for accurately separating a block copolymer according to the length of one of the blocks.

A convenient method for detecting compositional non-uniformity in block copolymers is centrifuging in a density gradient, obtained by using two solvents of different density. This technique allows the separation of fractions in which the concentration of polystyrene varies between very narrow limits.[66]

The molecular structure of block copolymers (i.e. the length and molecular-weight distribution of the blocks) can be controlled by introducing various lithium-organic compounds into the reaction mixture.[67] This process, too, is affected by the specific structure of the block copolymers, which differ substantially from those of homopolymers prepared under similar conditions.

To complete the description of the behaviour of block copolymers in solution we should note that the nature of the intermolecular interaction of the repeating units of different blocks, both with each other and with the solvent molecules, has been studied extensively in recent years. These interactions are very important in studies of the phase state of block copolymers in solution. Depending on the nature of the intermolecular interaction, which dictates the choice of a selective solvent or precipitant, dilute solutions can be replaced by concentrated solutions, the conformation of the chains in solution can be varied, and micellar structures in which the cores consist of blocks of either type can be obtained.

Another important aspect of the problem is the rheological behaviour of block copolymer solutions. In recent work on this topic the rheological behaviour of the solution (which depends on concentration) has been used to study the structure of block copolymers in solution. It is generally assumed that macroscopic networks whose nodes consist of domains of one of the blocks are formed in concentrated solutions. Concentration of the solution favours the formation of a lamellar structure, though in some cases the solution can show a mesomorphic structure. The macroscopic network can be broken down either by diluting the solution or by mechanical stresses. This approach can account for the rheological properties without postulating mechanical meshing of the chains in the solutions.

Thus block copolymers offer a convenient model system for studying the behaviour of polymer solutions, since they offer almost limitless possibilities of controlling the structure by varying the chemical arrangement of the blocks, their length and relative position, by varying the concentration of the solution, by using selective precipitants and solvents, etc. When solid samples are prepared from solutions of block copolymers all these aspects of their previous history can affect their structure and mechanical properties, as shown in the following Section.

III. STRUCTURE AND MECHANICAL PROPERTIES OF BLOCK COPOLYMERS IN THE SOLID STATE

The structure of block copolymers (and especially of block copolymers based on polystyrene and polybutadiene) was carefully studied even in the earliest work.[68-70] Structural

changes produced by increasing the content of polybutadiene phase in the polymer have been studied,[71] and various types of structure have been detected. At low concentrations of the polybutadiene fraction spherical domains are formed, dispersed in the polystyrene matrix, but at higher concentrations the polybutadiene forms cylindrical domains in a hexagonal packing arrangement. A further increase in the concentration of polybutadiene produces layer structures (alternating sheets of polybutadiene and polystyrene); the next stage is phase inversion, with cylindrical domains of polystyrene arranged in a polybutadiene matrix, and lastly the polystyrene domains become spherical at very high concentrations of polybutadiene (up to 80%).

The effect of the chemical structure of the blocks on the structure of binary block copolymers has been studied by low-angle X-ray scattering and by electron microscopy.[72] The thickness of the layers and of the layer structure in binary block copolymers increases if polystyrene is replaced by poly-α-methylstyrene or by poly-2-vinylnaphthalene (while keeping the molecular weight constant). The parameters of the layer structure are affected also by the thermodynamic properties of the solvents and by the concentration of the solutions.

The structure of block copolymers of polystyrene and polybutadiene has been studied[73] by varying the concentration of the vinyl component in the polybutadiene block from 10 to 60%. This change in chemical structure was shown to lower the degree of ordering of the system at the supermolecular level.

A theory which allows the size of the spherical domains to be calculated and their free energy to be estimated has been proposed.[74] This theory was tested by an experimental study of block copolymers of polystyrene and polybutadiene.

A thermodynamic analysis of a system composed of a block copolymer with cylindrical domains has been reported.[75] The size of the domains and the distance between them were calculated as a function of the composition of the block copolymer. Subsequently the thickness of the phase layers was also calculated.[76]

Various methods of studying the micro-phase separation of block copolymers in the solid state have been used, including X-ray structural analysis,[77] transmission electron microscopy,[78] and others.[79,80] Thus the nature of the domain structure in block copolymers of polystyrene and polybutadiene has been determined by low-angle X-ray diffraction and by transmission electron microscopy.[78] For polystyrene contents below 25% the films prepared from solutions in benzene (common solvent) and in cyclohexane (solvent specific to polybutadiene) contain spherical domains of polystyrene showing a high degree of segregation. Films prepared from solution in ethyl methyl ketone contain domains of polybutadiene dispersed in a polystyrene matrix.

The formation of block copolymer structures depends on the width of the molecular weight distribution (MWD) of the chains in the blocks. If the distribution is similar in each block (either narrow, or wide) and the concentration of the components is the same, the phase structure will also be approximately the same.[81] On the other hand if the polystyrene blocks have a narrow MWD and the polybutadiene blocks have a wide MWD the structure of the block copolymer becomes similar to that of a sample with a narrow MWD of all the components and a lower polybutadiene content. For the opposite relationship of the MWD of the blocks the structure is again similar to that of a sample with a narrow MWD of all the components, but this time with a lower concentration of polystyrene.[82] Because of its dependence on the MWD distribution of the blocks the structure of the block copolymers affects the properties of the material. A wide MWD favours the formation of a lamellar structure, which lowers the tensile strength and increases elongation. Samples with a narrow MWD display Newtonian flow over a wider range of shear rates than samples with a wide MWD.[82]

Micro-layering is essential to the development of toughening in block copolymers. This type of layering appears only when the molecular weight of the blocks exceeds a critical value. For example, for the block copolymers of polystyrene and polybutadiene the critical molecular weight of the polystyrene fragments was found[83] to be 2500, and that of the polybutadiene fragments 6000. At lower molecular weights no micro-layering was detected, and the toughening effect of the rigid blocks was absent. Conversely, in mixtures of polymers layering occurs at much lower molecular weights: for example, in a mixture of polystyrene and polyisoprene layering is observed at a molecular weight of polystyrene of 500.[84]

Changes in structure of block copolymers of polystyrene and polybutadiene as a result of heat treatment have long been known.[85] Annealing at temperatures above the glass transition point of the rigid block leads to equilibration in only a few minutes, whereas many hours are needed to reach equilibrium at temperatures below the glass transition point of the rigid block, in spite of the high elasticity of the sample as a whole. At higher temperatures the intensity of the low-angle X-ray reflexions decreases, and still further increase in temperature suppresses the reflexions completely, but the low-angle diffraction properties are fully restored by lowering the temperature.[86] Thus heating causes a gradual suppression of the phase structure of the block copolymer and a transition into a homogeneous system. However, the size of the transition regions stays almost constant during heating, i.e. an intermixing of different blocks appears to take place. This process is reversible, and micro-layering is restored by cooling.

Thus at high temperatures a transition from a two-phase to a single-phase structure may take place. In the case of block copolymers of polystyrene and polybutadiene this transition is observed[87] at 140–150 °C. The rheological properties of the samples change at the same time: non-linear mechanical behaviour is replaced by a linear behaviour, with a substantial decrease in elasticity. The existence of a transition from non-linear to linear rheological behaviour at 150 °C, caused by the breakdown of a multi-phase structure and the formation of a single-phase structure, has been confirmed calorimetrically.[88]

The specific structure of the block copolymers and the type of aggregation of the blocks allow us to produce some unusual structures in these polymers by special methods. Thus if samples of block copolymers of polystyrene and polybutadiene are oriented and then annealed at a relatively high temperature (for example, at 155 °C for 18 h) an oriented macroscopic lattice is formed: this is suggested by low-angle X-ray diffraction and electron microscopy measurements,[89] which detected the formation of a macroscopic lattice of polybutadiene cylinders in a polystyrene matrix. This type of micro-phase separation influences the properties of the system.

Different methods of analysis of the structure of oriented block copolymers[90] have indicated the possibility of a mesomorphic structure for block copolymers in this state. The rigid domains can form either cylinders or lamellae, and within the domains the macromolecules can be coiled in a bundle, as shown by measurements of double refraction and i.r. dichroism.

Previous studies of the orientation of the structure elements in block copolymers by low-angle X-ray diffraction,

electron microscopy, and other methods have been supplemented[91] by a study of the depolarisation of scattered light (in the polystyrene/polyisoprene block copolymer system). The method can detect small changes caused by the orientation of structure elements in block copolymers.

We shall now turn to an analysis of the structure and of the mechanical properties of block copolymers. The early work[92-94] was aimed mainly at the behaviour of these materials under uniaxial elongation conditions; hysteresis phenomena were also examined. The optico-mechanical properties of block copolymers[95] have been studied, and a detailed study of relaxation processes in these materials has been reported.[96] In both these investigations[95,96] an attempt was made to interpret the results by the classical theory of high elasticity, the rigid polystyrene domains being treated as filler particles incorporated in a polybutadiene matrix and not effectively involved in the relaxation processes. Some attempts to apply the classical theory of high elasticity to these systems were successful, but the general validity of the theory has not been confirmed.

The mechanical properties of block copolymers are influenced by the type of solvent used to prepare film samples for measurement. The influence of the properties of the solvent (measured by the solubility parameter) on the tensile curves and on the limiting strength and deformation properties is discussed in Ref. 97. A marked effect of the thermodynamic affinity of the solvent for each of the blocks on the shape of the tensile curves was noted in samples of polystyrene/polybutadiene block copolymers of different composition. As was subsequently established, the properties of the solvent from which the films are cast determine the hysteresis of the mechanical properties.[98]

The effect of the type of solvent on the structure and mechanical properties of block copolymers of polystyrene with hydrogenated polyisoprene or hydrogenated polybutadiene has been studied extensively.[99] Increasing the affinity of the solvent for the polystyrene fragments causes a transition from spherical to cylindrical polystyrene domains, though a lamellar structure is also possible for the block copolymers of polystyrene with hydrogenated polybutadiene. Increasing the anisotropy of the rigid domains causes a transition from samples with properties similar to those of unfilled rubber to materials showing induced elasticity.

The fracture mechanism in styrene–diene ternary block copolymers depends on the conditions used in their preparation and orientation. It has been shown[100] that crack propagation under tension at right angles to the axis of the flexible fragments causes brittle fracture, whereas if the cracks are propagated in a direction parallel to the bundles of flexible fragments plastic fracture is observed. The fracture surface is different in the two cases.

The block structure of these copolymers (as opposed to the random distribution of the units in conventional copolymers) affects not only the limiting mechanical and other properties of the material but also its compressibility. For example, for identical compositions the specific volume and compressibility of the random copolymer of styrene and butadiene are greater than those of the block copolymer of polystyrene and polybutadiene.[101]

The presence of rigid domains in block copolymers suggests a model in which flexible chains are held between neighbouring pairs of rigid domains: this model shows neither deformation nor swelling.[102] It can be used to calculate the elastic modulus, the partial molar free energy of swelling, and the dependence of the stress on the strain. When examining the effect of the structure on the mechanical properties of block copolymers it is important to allow for the polydispersivity of the sample and its influence on these properties.

By fractionating samples of block copolymers of polystyrene and polybutadiene it was shown[103] that the elastic modulus calculated from the stress–strain plot is slightly higher for the narrow fractions than for the original samples.

The prospective applications made possible by the control of the properties of ternary block copolymers through changes in the chemical structure of the blocks are demonstrated in Ref. 104. In this work polymers based on styrene, α-methylstyrene, ethylene sulphide, etc. were used as the rigid end blocks, whereas the flexible central blocks were polymers based on isoprene, butadiene, hexamethylenetrisiloxane, etc. In block copolymers of polystyrene and polybutadiene an increase in concentration of polystyrene was found to increase the strength of the material, but not in block copolymers of polystyrene with polyisoprene. In general good strength is achieved by using a high enough molecular weight for the end (polystyrene) blocks: according to these authors[104] it should be greater than 6000.

Hydrogenation of block copolymers based on polystyrene and polybutadiene causes a change in the mechanical properties of the samples: an increase in elastic modulus, etc.[105] Block copolymers show changes in properties also under the influence of radiation, though these changes reflect the special structural features of the materials.[106] Increasing the concentration of polybutadiene fragments in the block copolymer makes the properties more sensitive to the radiation: the strength decreases, the hardness and stiffness increase, the thermal diffusivity increases, and the swelling tendency is affected. All these effects arise from the cross-linking of the polybutadiene blocks, which thus cease to be inert fillers and become active sites in the network.

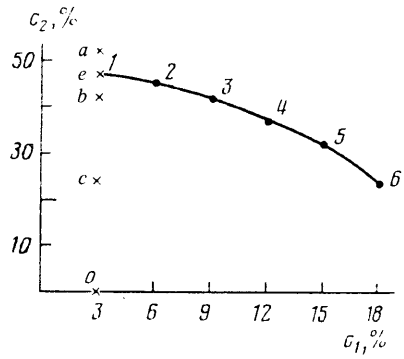


Figure 1. Nephelometric titration curve for solutions of the block copolymer of polystyrene and polybutadiene in benzene against iso-octane: c_1 is the concentration of polymer, c_2 is the concentration of iso-octane, *1–6* are compositions on the nephelometric titration curve, the crosses denote the compositions used to prepare the samples for these experiments.[115]

We should again stress the fact that changes in the structure of block copolymers produced by varying the type of solvent during film preparation can result in changes in properties as substantial as those produced by varying the chemical structure of the copolymer. The shape of the tensile curves is affected not only by the composition of the

block copolymer but also by the thermodynamic properties of the solvent from which the sample is cast.[107,108] Controlling the structure of the block copolymer by varying the composition of the solvent is a convenient method of minimising internal stresses in coatings.[109]

In studies of the adhesion strength of these materials the properties of the surface layers of block copolymers have been monitored by the changes in resonance frequency of a quartz prism on which a layer of polymer had been deposited. According to these experiments[110] an increase in the concentration of polystyrene decreases the number of bonds to the substrate and lowers the adhesive strength.

So far our discussion has been confined to the effect of the structure of the block copolymers on the limiting strength and deformation properties. Let us now examine the relaxation properties of block copolymers under static conditions.

The structure of block copolymers makes these materials specially suitable for studies of the mechanical properties of two-phase systems. The effects of physical ageing on the relaxation properties of block copolymers of polystyrene and polybutadiene have been studied, and the dependence of the time to reach equilibrium on the duration of the annealing treatment has been determined.[111,112] The prediction of the behaviour of polymers under creep conditions from stress relaxation data has been demonstrated[113] for block copolymers of polystyrene and polybutadiene. The strongly non-linear viscoelastic behaviour of these materials is noteworthy.

The most detailed studies of the relaxation properties of block copolymers of polystyrene and polybutadiene are reported in Refs.114 and 115. The samples used in this work contained between 30 and 62% of polystyrene, and they had a wide range of properties. As was stated above, these block copolymers are a convenient medium for the study of the effect of polymer structure on the viscoelastic behaviour of the sample. The structure of these copolymers can be easily changed during the preparation of films from solutions by varying the composition of the solvent, which can be either a mixture of a solvent and a selective precipitant for one of the blocks or a homogeneous solvent with different solubility parameters for the two blocks. The solvent most commonly used in this work is benzene,[114,115] while iso-octane has been used as a selective precipitant for polystyrene blocks. A nephelometric titration curve was used to determine the composition of the solvent medium (Fig.1). The region below the curve corresponds to true solutions, the region above the curve to dispersions. The points in Fig.1 give the composition of the solvent medium used in the preparation of samples of block copolymer film.

The stress relaxation curves for block copolymer films prepared from solvent media of different composition were also determined in the same investigation.[114,115] The measurements were made in the strain region between 5 and 600% at temperatures between −30 and +80 °C. It was found that the addition of a selective precipitant for polystyrene

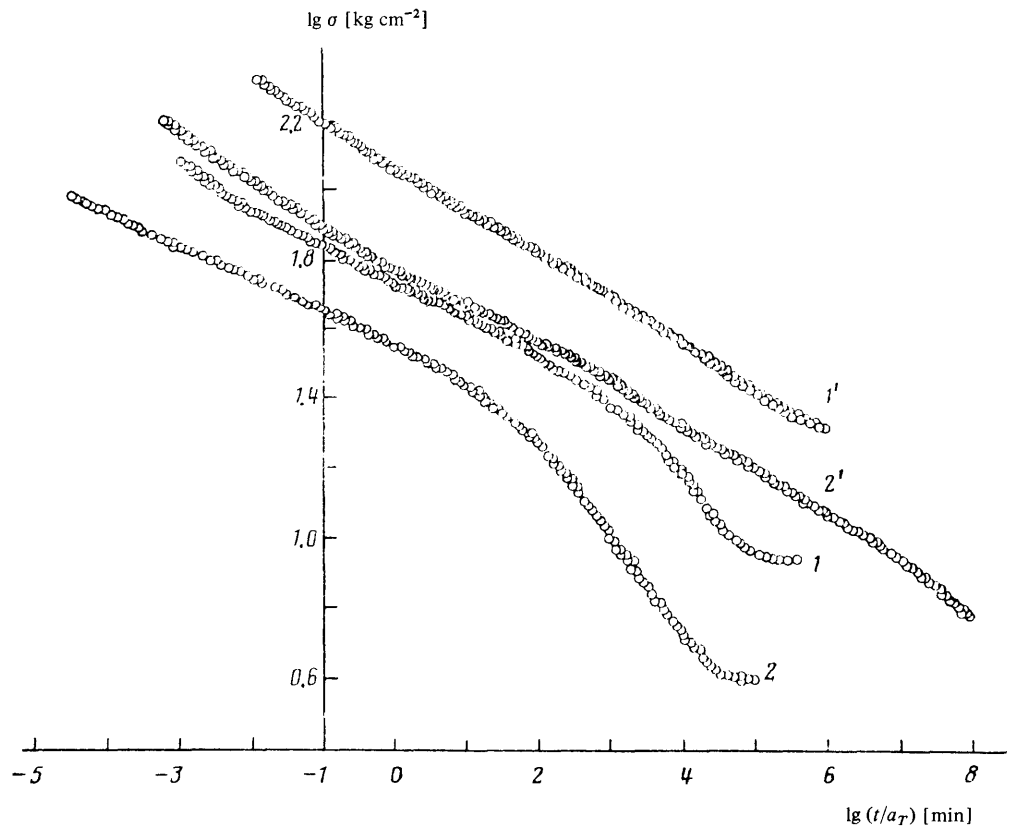


Figure 2. Generalised relaxation curves for deformations by 10% (*1*, *2*) and by 400% (*1'*, *2'*): *1*) and *1'*) are for samples formed from solution, *2*) and *2'*) for samples formed from a dispersion[115] (a_T is the shift factor).

blocks accelerates the stress relaxation, and at the same time the equilibrium elastic modulus is lowered, the effects being observed at all temperatures. Irrespective of the initial concentration of the block copolymer in the mixture of solvent and precipitant, the films formed from a true solution show a much greater equilibrium elastic modulus and relaxation time than films prepared from dispersions.[115] A sharp decrease in equilibrium modulus and in relaxation time can be induced by forming the film from a mixture of solvent and precipitant of composition close to the phase separation curve but on the true solution side.

Fig. 2 shows, as an example, the generalised relaxation curves for films prepared from a solution (point "0" in Fig. 1) and from a dispersion (point "a" in Fig. 1). The generalised curves were obtained by shifting the stress relaxation curves along the lg t axis. The generalised curves for samples prepared from dispersions are invariably found in the region of lower stresses than those for samples prepared from solutions. This may be due to coiling of the polystyrene blocks as a result of the addition of a selective precipitant, with formation of a compact structure which does not contribute so effectively to the relaxation process.

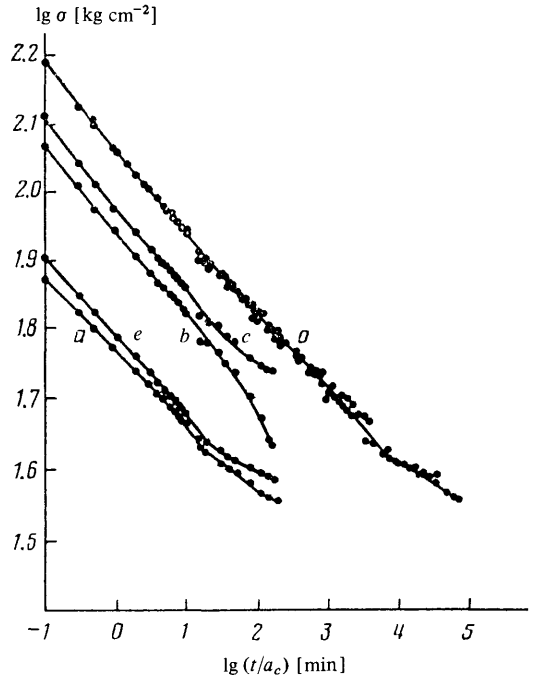


Figure 3. Initial and generalised stress relaxation curves for films prepared at different concentrations of the selective precipitant, ε = 400%, curves numbered as in Fig. 1.[115]

This conclusion is consistent also with the relaxation curves for samples prepared from media with different concentrations of the selective precipitant. These curves can be reduced to a single curve, shown in Fig. 3, by a shift along the lg t axis. In this case the reduced parameter is not the temperature but the concentration of selective precipitant. The plot of the logarithm of the shift factor lg a_c against $(c - c_0)$, where c is the concentration of the selective precipitant and c_0 is the concentration used in the reduction, has the characteristic shape shown in Fig. 4, indicating the presence of a narrow range of concentrations of the precipitant in which the relaxation processes are strongly accelerated. In the case of this particular block copolymer (containing 62% of polystyrene) the critical concentration of precipitant is 45%.

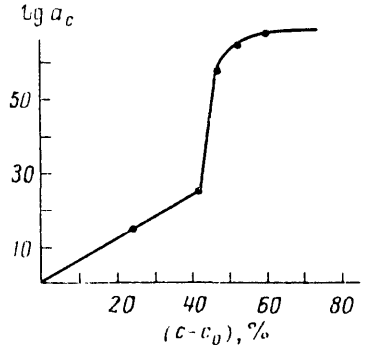


Figure 4. Plot of lg a_c against $(c - c_0)$.[115]

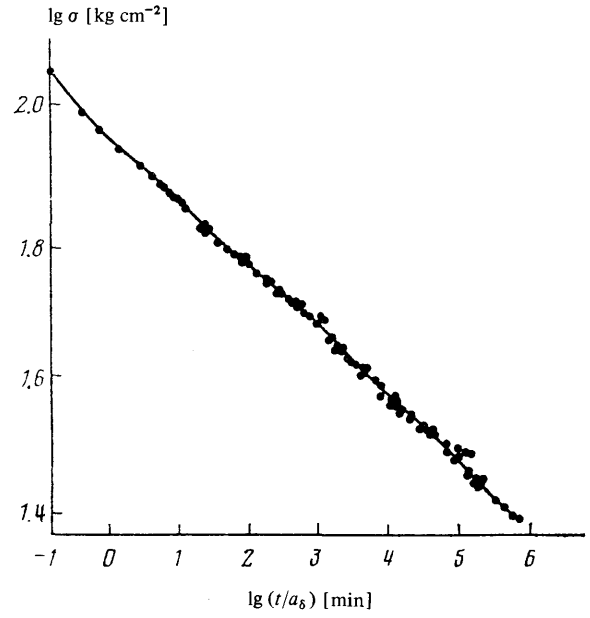


Figure 5. Generalised stress relaxation curve for samples formed from different solvents (ε = 10%).[115]

The relaxation properties of a block copolymer can also be controlled by preparing samples from solvents with different solubility parameters δ. The initial and the generalised relaxation curves for samples prepared from solvents with different values of δ are shown in Fig. 5. Increasing the δ value of the solvent to a value equal to or greater than the characteristic value for the polystyrene blocks causes a

marked increase in the relaxing and the equilibrium stresses. Hence by changing the solvent medium we can substantially affect the relaxation properties of block copolymers, and we can lower, or raise, the strength of the equilibrium stresses, i.e. we can control the degree of completion of the relaxation process.

To generalise this conclusion the relaxation curves (corresponding to different values of δ) were shifted along the $\lg t$ axis to merge into the previously obtained generalised curve (see Fig. 5). The dependence of the shift factor $\lg a_\delta$ on $(\delta_0 - \delta)$ is shown in Fig. 6, where δ_0 is the solubility parameter for dioxan. As the solubility parameter δ increases, the shift factor decreases.

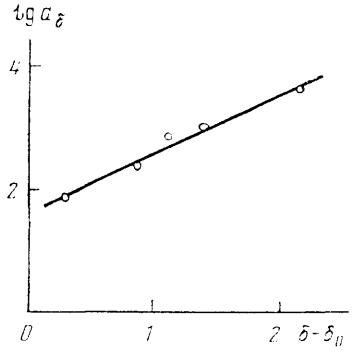


Figure 6. Plot of the shift factor $\lg a_\delta$ against $(\delta - \delta_0)$.[115]

Thus the study[114,115] of the mechanical (relaxation) behaviour of block copolymers has revealed extensive prospects for controlling the relaxation properties of these materials, depending on the previous history of the formation of the film samples from solution. Obviously, studies of the relaxation properties allow us to reach definite conclusions as to the activity of the rigid particles formed by the polystyrene domains which act as a strength-enhancing filler.

The durability and creep properties of polystyrene and polybutadiene block copolymers under conditions of uniaxial tension are discussed in several papers.[116–118] Both reversible and irreversible deformation is observed in the creep process, and the durability is decreased by an expression which is characteristic of rubber. The activation energies of the fracture, creep, and viscous flow processes are identical, suggesting that all three processes take place by the same mechanism (involving the breakdown of the domain structure).

The relaxation properties of block copolymers have been studied also in melts. The relaxation of the stresses in a melt of the block copolymer of polystyrene and polybutadiene after stopping the deformation has been measured.[119] It was found that the stress decays not to zero (as in linear elastomers based on homopolymers) but to some final value which is greater, the shorter the deformation time of the melt. Hence the evidence for a network structure is present also in the melt. The existence of a final stress was detected also in a study[120] of stress relaxation in block copolymers at relatively high temperatures. This behaviour of block copolymers under conditions of stress relaxation in the melt is attributed to the formation of star-shaped structures after the initial breakdown of the domain structure originally present in the melt by the action of the shear deformations.[121]

The relaxation properties of block copolymers under conditions of dynamic mechanical interaction have been studied in depth. We shall not dwell on any particular investigation, but we shall merely point out that in addition to the strengthening effect of the rigid blocks we find two maxima in the temperature dependence of the slope of the mechanical losses[122–125] for many of these copolymers. There is also a change in the temperature dependence of the shift factor, detected by applying the temperature–time superposition principle to the analysis of the experimental results.[126,127] Deviations from the usual dependence, described by the Williams–Landel–Ferry equation, are observed at temperatures above the glass transition temperature of the polystyrene phase of the block copolymer of polystyrene and polybutadiene.

As in the case of the parameters of the static mechanical properties, the type of solvent used in the preparation of the sample has an important effect on the results of dynamic mechanical tests. Thus the dependence of the dynamic mechanical properties of films of a ternary block copolymer of polystyrene, polyethylene, and polybutene on the solubility parameter of the solvent used in casting the film has been studied.[128] Because of the better dispersion of the polystyrene domains and of the possibility of contacts between these domains the use of a good solvent causes a large increase in the accumulation modulus of the system. If a poor solvent is used the polystyrene blocks are isolated and cannot form mutual contacts: as a result, the relaxation of the stresses is rapid, and the accumulation modulus decreases.

The structure of block copolymers and the tendency of their fragments to aggregate lead to an unusual effect of the rate (or frequency) of the mechanical interaction and of the temperature, and also of the magnitude of the mechanical stress, on the dynamic mechanical properties of the samples. Thus at low shear rates the block copolymers of polystyrene and polybutadiene behave as dispersed systems showing marked thixotropy.[129] At high shear rates the viscoelastic behaviour of these systems is determined mainly by the polybutadiene matrix. Similar effects are observed at high shear stresses. The viscoelastic properties of block copolymers of polystyrene and polybutadiene at low temperatures are similar to those of rubber. At high temperatures (above the glass transition temperature of the polystyrene fragments) even low-amplitude deformations produce a small amount of viscous flow in spite of the substantial residual aggregation of the polystyrene blocks mentioned above.

A similar study by a different method is reported in Ref. 130. The samples were block copolymers of polystyrene and polybutadiene in which the molecular weight of the polystyrene blocks was much lower than that of the polybutadiene fragments. Measurements of the dynamic shear modulus and of the dynamic viscosity over a wide range of temperature showed that the temperature–time superposition principle applies in these systems, the temperature dependence of the dynamic viscosity dropping sharply at 142 °C (in the low-frequency region). At high frequencies a different behaviour is observed. From these results the authors concluded[130] that a critical temperature exists for block copolymers at which the domains formed by the rigid blocks begin to collapse and the material becomes more homogeneous.

Detailed studies of the dynamic mechanical properties of ternary block copolymers of the ABA type of different chemical structure have been reported.[131] The end blocks

were polystyrene, and the central block was polybutadiene, polyisoprene, polydimethylsiloxane, etc. Most of the work was carried out at temperatures above the glass transition temperatures of both blocks. The main difference between the mechanical behaviour of the block copolymers and of the homopolymers is a higher value of the dynamic viscosity, due to the aggregation of the polystyrene domains. This aggregation is found even at temperatures above the glass transition temperature of polystyrene. The aggregation is less evident in block copolymers containing polyisoprene as the central block. An analysis of the dynamic mechanical behaviour of these systems has shown that differences between the solubility parameter for the central block and for the end blocks play a major role.

The dynamic mechanical behaviour of block copolymers of polystyrene with polybutadiene, hydrogenated polybutadiene, polyisoprene, hydrogenated polyisoprene, and polydimethylsiloxane has been fully analysed.[132] Both binary and ternary block copolymers were studied. The work was aimed mainly[132] at demonstrating the influence of the molecular weight distribution of the block copolymers on the relaxation transitions. Two relaxation transitions were observed, corresponding to the devitrification of the two phases, and the temperatures of these transitions were shown to depend on the type of molecular weight distribution. The high-temperature transition takes place at a lower temperature than in homo-polystyrene.

The relaxation properties of block copolymers have been studied not only by dynamic mechanical methods but also by various other physical methods: dielectric, i.r. spectroscopic, etc. Careful attention is currently paid in studies of the dielectric properties of polymers to processes associated with the boundaries of structural formations. In this respect block copolymers are specially interesting, because they are micro-heterogeneous systems. A theoretical and experimental study[133] of dielectric relaxation has shown that at low frequencies the experiment is adequately described by the theory, though allowance is needed for both the bulk concentration of components and the type of supermolecular structure in the calculation of the dielectric parameters.

Transitions resulting from molecular mobility in the interphase regions have also been detected by the positron annihilation method.[134]

Transition in block copolymers and in their solutions are reliably observed ultrasonically, using the form of the adsorption and the velocity of the ultrasound.[135] Two transitions, corresponding to the devitrification of the polybutadiene and polystyrene phases, were observed in the initial block copolymers. The same transitions were observed in the swelled samples, but in this case the transitions were shifted towards lower temperatures. In solutions high-frequency attenuation is enhanced, due to the presence of micellar formations. The study of the acoustic properties of block copolymers of polystyrene and polybutadiene has shown[135] that the glass transition temperature (which is related to the polybutadiene phase) depends on the concentration of the polystyrene component and on the method of preparation of the sample. Extruded samples show a characteristic increase in glass transition temperature.

The relaxation properties of block copolymers have also been studied by thermally stimulated current and thermoluminescence methods.[137]

In general, each of the components of a block copolymer can influence the glass transition temperature of the other component, which depends on the length of the block. An analysis of this effect[138] has clarified the dependence of the glass transition temperature of the polystyrene component on the length of the polystyrene block. The second components of the block copolymers were polyisoprene and polydimethylsiloxane blocks, whose compatibilities with polystyrene are different. Nevertheless the decrease in glass transition temperature caused by a decrease in the length of the polystyrene block was about the same in the two cases. This suggests that the change in glass transition temperature is not always determined by the level of compatibility and may also depend on other factors (for example, internal stresses).

The relaxation properties of block copolymers have also been studied (as was mentioned above) by i.r. spectroscopy.[139] The micro-heterogeneous structure of the block copolymers results in a non-monotonic decrease in optical density with increase in temperature.

A detailed analysis of relaxation transitions in block copolymers of polystyrene and polybutadiene has been carried out by a dilatometric method.[140] The character of the transitions was found to depend not only on the molecular weight and composition of the block copolymer but also on the previous thermal history of the sample. Thus in samples containing 44 wt.% of polystyrene the transitions were observed at 0.87 T_g and (0.92–0.95)T_g. Heating the samples to 40 °C causes these transitions to disappear, and annealing at 55 °C induces a new transition at $T = 0.90T_g$. All these effects have been ascribed[140] to ordering of the inter-phase regions during annealing.

It is interesting to compare the dilatometric characteristics of block copolymers with those of mechanical mixtures of homopolymers having the same composition.[141] Whereas several transitions are detected at temperatures below the glass transition temperature of polystyrene, no relaxation processes are observed in mixtures of polystyrene and polybutadiene.

Several papers discuss the rheological behaviour of block copolymers, which is important for optimising the technological processing of these materials. The special rheological behaviour of block copolymers is ascribed[142] to the formation of a stable physical network and to the possibility of transition to the highly elastic state at high shear rates (of course, this refers to a melt of the block copolymer at high temperature). During the technological treatment of block copolymers of the SKS type, the only changes are a slight swelling and a small shrinkage.

The rheological properties of ternary block copolymers of polystyrene and polybutadiene have been compared with those of polybutadiene rubber.[143] The most significant result was that the block copolymer shows a non-linear dependence of the logarithm of the viscosity on the reciprocal temperature, which cannot be described by the conventional relations which apply to homopolymers.

The rheological behaviour of ternary block copolymers has been described by a model[144] in which the interfacial layer between the matrix and the domains embedded in it plays the main role in controlling the rheological properties. The effect of structure on non-Newtonian flow, phase inversion, etc. can be described by introducing three segmental friction coefficients.

The rheological behaviour in the pre-stationary region of the deformation of block copolymers of polystyrene and polybutadiene has been studied.[145] These systems are characterised by an anomalous dependence of the limiting shear strength on the shear rate: under these conditions an important role is played by orientation effects.

Considerable effort is being devoted to the development of micro- and macroheterogeneous systems free from the brittleness found in the homopolymers which form the rigid domains in block copolymers. A recent review[146]

of this topic discusses, in addition to the traditional methods of preparing block copolymers and their mixtures with homopolymers, some original approaches such as polymerisation of the monomer from one of the blocks in a solution of the complete block copolymer. Of course, this method applies to the formation of composite materials, which can also be prepared by other methods.

As was stated above, block copolymers offer very attractive possibilities of controlling the properties of synthetic materials. Even more important prospects of controlling the structure and properties of these materials are created by mixing block copolymers with homopolymers of various structures. Whereas in block copolymers we observe micro-phase separation of the system and phase inversion, in the case of mixtures of a block copolymer with homopolymers having the same structure as the fragments of the block copolymer we find both micro- and macro-layering.[147] The nature of the phase separation depends mainly on the difference in molecular weight between the homopolymer and the corresponding blocks, and also on the composition of the components of the mixture. If the molecular weight of the homopolymer is approximately equal to (or smaller than) the molecular weight of the corresponding block the homopolymer dissolves in the blocks of the copolymer. In the opposite case we observe macro-layering, and the homopolymer forms a separate phase, while the corresponding blocks of the copolymer distribute themselves at the boundary of this phase. In the first case (micro-heterogeneity) the specific impact viscosity stays low. The best result was obtained[147] for a micro-heterogeneous system in which the particles of the copolymer are dispersed in the polystyrene matrix.

As we have already pointed out, mixtures of block copolymers with homopolymers having a constitution analogous to that of the corresponding blocks are being intensively studied at present. The properties of these systems are sensitively dependent on the micro-domain structure of the block copolymers and on their deformation mechanism.[148] One possible mechanism is the formation of micro-cracks under tension in the rigid domains in the block copolymer (for example, in the polystyrene domains), which requires a large expenditure of energy. Another mechanism consists in the formation of a macroscopic neck in the rigid component of the block copolymer: this mechanism has been confirmed in samples with a micellar structure. A successful combination of a block copolymer and a homopolymer should produce a system with impact-resisting and other useful properties. Thus the rheological behaviour of mixtures of polystyrene and ternary block copolymers of polystyrene and polybutadiene under shear conditions is typical of mixtures of incompatible polymers, the addition of a small amount of the block copolymer to the polystyrene causing an increase in the viscosity and the elasticity of the melt.[149]

The structure and the dynamic mechanical properties of mixtures consisting of the normal block copolymer of polystyrene and polybutadiene (SBS type) and of a branched block copolymer have been studied.[150] The mixtures were prepared in a way which kept the concentration of polystyrene constant (75%) but allowed the block length to be varied. The structure of the samples can be controlled during preparation so as to vary not only the mechanical properties and their anisotropy, but also the glass transition temperature of the rubber-like component embedded in the polystyrene matrix. In general the use of mixtures of block copolymers offers very wide prospects of controlling their structure: samples containing structure elements varying from spherical to rod-like have been obtained in this way.

Macro-heterogeneous compositions based on block copolymers of polystyrene and polybutadiene of the SBS type and containing prescribed amounts of polystyrene as a filler can be prepared by the pressure casting method.[151] Optical and microscopic studies have shown that the addition of polystyrene leads to phase layering of the system. Composite materials based on block copolymers are conveniently prepared by using rollers or rubber mixers. Changes in composites based on thermoelastoplastics and polystyrene have been studied by a thermomechanical method and by hydrostatic weighing.[152]

Ternary block copolymers have been mixed with binary block copolymers in order to control their physical and mechanical properties.[153]

Composite materials can also be prepared by adding various fillers to block copolymers (for example, technical carbon). The effective density of nodes in the three-dimensional network of block copolymers of polystyrene and polybutadiene has been shown to increase with the concentration of technical carbon added to the block copolymer.[154] Increasing the dispersion of the filler has the same effect.

Block copolymers have been used to prepare vulcanisates by cross-linking hexachloro-*p*-xylene in the presence of metal oxides.[155]. The presence of these oxides allows the formation of coordination and adsorption bonds, which raise the strength of the vulcanisates. The relaxation properties of these materials have also been studied,[155] and shown to be controllable through changes in the characteristics of the bonds.

We shall conclude this discussion by reviewing the work on structural changes in block copolymers during deformation. Both direct structural methods and thermodynamic approaches have been used in this analysis.

A detailed study of the structural changes accompanying the deformation of block copolymers of polystyrene and polybutadiene is reported in Ref. 156. In the first elongation cycle the dependence of the stress on the deformation has the characteristic shape found in glassy polymers (the concentration of polystyrene was 48%). In a repeated elongation cycle the stress–strain relationship is typical of elastomers. The reason for these changes is that the first elongation causes breakdown of the initial lamellar structure to give small particles, so that the sample is converted into a polybutadiene matrix filled with dispersed particles. After a rest period the sample tends to revert to its initial structure, and heat treatment at 59 °C (which is well below the glass transition temperature of polystyrene) restores the initial structure almost completely. This effect suggests[156] the presence of a substantial inter-phase layer containing both polystyrene and polybutadiene blocks: this structure could cause a decrease in the glass transition temperature of polystyrene. However, in the absence of dynamic mechanical data the suggested mechanism[156] can only be tentative.

Electron microscopy and low-angle X-ray diffraction methods have been used to study the structural changes accompanying the transition from the "hard" to the rubbery state during mechanical elongation of block copolymers of polystyrene and polybutadiene and of their mixtures with polystyrene.[157–159] The results are similar to those discussed above: regular deformation of the lamellae is observed in the initial stages of elongation (up to 5%), then the lamellae undergo shear, fracture, reorientation, and collapse successively, and in the last stages of collapse a structure with polystyrene domains uniformly distributed in the polybutadiene matrix is produced.

A similar result was obtained in a study of the deformability of block copolymers of polystyrene and

polybutadiene containing different amounts of polystyrene.[160] The polybutadiene blocks contained fragments with *cis*- and *trans*- structures. The breakdown of the domain structure of the block copolymer and its dispersion in the polybutadiene matrix were again observed; annealing restored the initial structure and properties.

The break-up of the cylindrical domain structure formed by polystyrene blocks is observed most clearly during elongation of the block copolymers in the direction of the cylinder axis.[161] The same behaviour is observed in rheological studies.[161] In the presence of a small mechanical stress the domain structure of the block copolymer is preserved, but above some critical stress the giant networks formed by the domains begin to collapse. This produces a break in the plot of shear stress against shear rate. When the domain structure is fully broken down the viscosity of the block copolymer is described by the normal flow curves, and the temperature dependence of the viscosity by the Williams–Landel–Ferry equation.

The simultaneous application of small-amplitude dynamic deformations and large static deformations produces a mechanical loss peak at the point where the initial structure of the block copolymer is broken down by the static deformation.[163] Under these conditions the height of the peak increases with time, because the breakdown of the initial structure affects increasingly deep layers. The destruction of the initial structure of the block copolymer is accompanied by the formation of an oriented structure as a result of the development of large highly elastic deformations in the polybutadiene matrix.[164]

The deformation behaviour of block copolymers of polystyrene and polybutadiene (SBS type) has been studied[165] with allowance for the anisotropy of the structure of the material. Samples having a structure of the "single crystal" type were studied, i.e. samples in which the cylinders consisting of polystyrene domains were packed in a parallel arrangement in the polybutadiene matrix. As a result, the deformation behaviour in extension was different in directions parallel to and perpendicular to the cylinder axes. Under extension at right angles to the cylinder axes the cylinders (being hexagonally close packed) undergo affine deformations, like the sample as a whole. This deformation is reversible, but when it exceeds 10% we observe a well defined irreversibility attributed to the formation and development of cracks in the sample. In parallel deformation the fluidity limit is reached at low elongations, and the Mullins–Patrikeev effect is clearly shown. After a period of rest (especially with annealing) the sample becomes more elastic, and the effect can be explained by the dispersion of the cylinders after the first elongation and their re-establishment after the rest period. Thus the system displays thixotropic properties.

Structural changes during the deformation of isotropic and of oriented polymers have been compared.[166] In oriented samples, having an initial structure of the single crystal type, deformation in a direction perpendicular to the cylinder axes initially distorts the crystalline arrangement and then produces bends in the crystal (at the weakest points). The crystals (in the shape of a flat zig-zag) are deformed at the bends during subsequent extension. On the other hand if the deformation is applied in a direction parallel to the cylinder axes it causes the cylinders to break into residues about 1000 Å long. Under these conditions, and for small elongations, the orientation of the initial structure elements (for example, the cylinders) is retained, since the elongation is achieved by the deformation of the highly elastic matrix.[167]

The detailed thermodynamics of the deformation and fracture processes of block copolymers of polystyrene and polybutadiene have been investigated for systems containing 40–50% of the polystyrene phase, and the special features of the thixotropic processes in the solid phase, whose rate is strongly temperature-dependent, have been studied.[168–171] An analysis of the energy balance of the softening processes using a high-precision calorimeter showed that the softening caused by deformation depends on the break-up of the polystyrene phase, especially during the initial stages of the process, and that the process is accompanied by an increase in the internal energy of the sample. During the thixotropic recovery period the stored energy is dissipated, and the recovery process itself (as stated above) is strongly temperature-dependent: it goes to completion in a few seconds at 100 °C, as opposed to 5–10 days at room temperature.

The deformation calorimetry method has been used to show that at high deformations the increase in stress is due to the acceptance of the load by the polystyrene domains, and to the deformation of these domains, and not to the limited extensibility of the polybutadiene chains. On the whole, the morphology of the polystyrene phase is the main controlling factor in the deformation behaviour of block copolymers of polystyrene and polybutadiene.

The changes in lamellar structure caused by the elongation of block copolymers of polystyrene and polybutadiene, and their elimination by annealing, have been studied thermodynamically.[172] The thermodynamic properties of the materials were calculated theoretically by introducing an approximation[173] in which the space between the domains is assumed to be much narrower than the domains themselves. With this assumption the free energy could be calculated as the sum of the following quantities: the energy associated with the surface tension, the energy associated with the topology of the blocks at the interface, and the change in entropy. In this case the entropy decreases, since the samples should have a uniform density over the entire volume. By calculating the free energy of the system and minimising it a theoretical estimate of the periodicity and of the disposition of the domains could be obtained.

The influence of structure on various properties (hardness, strength, thermo-mechanical characteristics) has been studied with star-shaped block copolymers of polystyrene and polybutadiene.[174] The main effort was devoted to a comparison of the initial properties with those of deformed samples. As in other work it was found[174] that in the first experiment the star-shaped block copolymers exhibited the phenomenon of induced elasticity: the effect was more clearly marked than in linear thermoelastoplastics (20% higher than the Shore hardness). At the second deformation the polymer becomes more elastic, but its initial structure and properties can be restored by annealing. These phenomena are attributed[174] to the formation of an interfacial transition layer consisting of polystyrene bridges, which are broken during the first deformation cycle.

The properties of block copolymers have been studied[175] at relatively low temperatures and their structural transitions have been examined in depth.

Thus the main areas of research on the structure and properties of block copolymers in the solid state are the application of the latest physical methods for studying structures (low-angle X-ray diffraction, transmission electron microscopy, thermodynamic analysis, positron annihilation, ultrasonics, etc.), and also wide-ranging rheological studies covering large changes in temperature, stress, and deformation rate. Two series of papers on the latter topic deserve special mention. One series[116–118] deals

with the rheological behaviour of block copolymers under uniaxial elongation conditions. This work highlights the single mechanism common to fracture, creep, and viscous flow processes in block copolymers, involving the collapse of the initial domain structure. The other series of papers describes a study of the mechanical behaviour of these materials by deformation calorimetry, which has demonstrated the fundamental effect of the domains formed by the rigid blocks on the shape of the tensile curve.

To review the thermodynamic approaches to the analysis of block copolymer structures we must stress the problem of determining the parameters of the effective network by using the expressions of the classical theory of high elasticity. In principle the size of the fragment between the points of the network M_C can be determined if the equilibrium elastic modulus E_∞ is known. In the earlier work the quantity M_C had been found to coincide in many cases with the molecular weight of the flexible (for example, polybutadiene) blocks. It is important to establish the correct way of determining the equilibrium elastic modulus in the case of a block copolymer. We know that in lattices with chemically defined nodes the equilibrium stress (elastic modulus) can be determined from the stress relaxation curve, but the relaxation process should not only have gone to completion at the given temperature (for a given deformation) but the stress should also have been allowed to reach its equilibrium value after upward and downward temperature excursions. In block copolymers the nodes of the network are the domains formed by the rigid blocks, and an increase in temperature can cause softening of the nodes and substantial changes in the relaxing stress. Therefore the correct determination of the equilibrium stress in block copolymers remains an open problem, though experimental data convincingly demonstrate[114,115] the important influence of the rigid domains on the rheological properties and show that these domains do not act as an inert filler but take an active part in the formation of the set of relaxation properties of block copolymers, including those observed in studies by the swelling method.

IV. DETERMINATION OF THE STRUCTURE OF BLOCK COPOLYMERS BY THE SWELLING METHOD

The swelling (or sorption) method has been used to determine the structure of block copolymers in two variants. Firstly, the effective length of the flexible (for example, polybutadiene) blocks has been determined, and secondly the method has been used to study the structural changes accompanying the swelling, and the influence of the method of preparation and of the previous thermal history of the sample on its sorption characteristics.

Several procedurally important aspects must be included in the analysis of block copolymer structures by the sorption method.[176] The first is the dependence on the thickness of the sample of the diffusion coefficient D determined from sorption and desorption data. For example, the parameter D increases from 10^{-8} to 30×10^{-8} cm^2 s^{-1} as the thickness of a film of the block copolymer of polystyrene and polybutadiene is increased from 50 to 300 μm.[176] The second special feature is the dependence of D on the type of substrate used to prepare the film. Lastly, annealing of the sample also tends to increase the value of D.

There have been many attempts to determine the length of the elastic block from data on the swelling behaviour. In all this work swelling was allowed to take place in a solvent which is selective towards the elastic blocks. In some cases satisfactory agreement between calculated and experimental lengths of the elastic block (for example, polybutadiene) was obtained,[177,178] but in other cases the discrepancy was serious.[179–181]

The Flory–Huggins interaction parameters have been determined by sorption measurements for styrene–butadiene copolymers of different composition.[182] In these determinations, it is important to remember that the segmental mobility of the polybutadiene blocks in the copolymers is smaller than the chain mobility in the initial polybutadiene.[183] This is not surprising, since the transport process is obstructed by the polystyrene domains, which are impervious to the solvent vapour.

The changes in structure of ternary block copolymers during swelling and desorption, and the re-establishment of the initial structure by annealing, have been studied by the low-angle light scattering method.[184] Rods of the polystyrene blocks oriented at different angles retain their orientation during swelling in iso-octane, but changes are observed after evaporation of the solvent. This behaviour is characteristic of block copolymers of polystyrene and polybutadiene, but not of the analogous copolymers of polystyrene and polyisoprene.

The effect of the solvent used to cast the block copolymer samples on the sorption and desorption of *p*-aminoazobenzene has been studied. The differences in structure of the block copolymer resulting from changes in the type of solvent (for example, phase inversion) are reflected by changes in the diffusion coefficient and in the temperature dependence of the rate of desorption. The large increase in the rate of desorption at higher temperatures is attributed to devitrification of the polystyrene phase[185] because of the changes in the glass transition temperature of polystyrene as a function of the type of solvent used in the preparation of the film.

The properties of block copolymers of polystyrene and polybutadiene in film form depend on the substrate used in the preparation of the sample. This dependence is clearly seen in experiments on the sorption of cyclohexane vapour in film samples deposited on glass, Teflon, or mercury. The rate of approach to sorption equilibrium is determined by the type of substrate used. Films prepared on solid substrates develop internal stresses which are thought[186] to influence the packing density of the macromolecules and hence the diffusion coefficient. However, we should note that the mechanical stress itself can affect the diffusion coefficient through its influence on the relaxation time (see below).

In another paper from the same laboratory[187] the effect of the structure of block copolymers of polystyrene and polybutadiene on the sorption curves and on D is discussed for a sample containing 25% of polystyrene. The sorbate was iso-octane. The structure of the samples was varied by using different substrates (glass, mercury, Teflon) for film preparation, and also by varying the thickness of the films. The diffusion coefficient was found to depend on the size and on the number of the polystyrene domains in the block copolymer. Therefore the sorption experiments are an effective method for the analysis of the structural changes in block copolymers.

A detailed study[188] of the relaxation mechanism of the swelling of polymers, which determined the kinetics of the process, is relevant in this context. It is assumed that the diffusion of low-molecular liquids or vapours in polymers is determined not only by the penetration of the sorbate molecules into the pores of the polymer but also (and to a large extent) by conformational rearrangements of the macromolecules, i.e. by the relaxation phenomena which accompany the diffusion process. Under these conditions we observe degeneracy of the long relaxation times. The

suggestion that the swelling of polymers is related to conformational rearrangements in the macromolecules and to the degeneracy of long relaxation times was first put forward in Ref. 189. It has since been confirmed by calculations and experiments.[188]

The more recent work[188] is based on a mathematical model of the process in which the viscoelastic polymer medium responds to interactions with the sorbate molecules. The associated model of the viscoelastic body consists of two Aleksandrov–Lazurkin elements connected in parallel; this model was used in calculations of stress relaxation and creep processes for these materials.

The same workers[188] had previously introduced the concept of a time-dependent diffusion coefficient, and had obtained a solution of the differential equation for Fick's second law in which the diffusion coefficient is expressed in terms of Einstein's system of equations for the Brownian motion (which includes the velocity of the diffusing species). Having determined this velocity from the proposed model the authors[188] found the time dependence of the diffusion coefficient and used it to calculate the dependence of the mass of the diffusing species on time by the expression

$$\frac{M(t)}{M(\infty)} = A_1(1 - e^{-t/\theta_2^*}) + A_2(1 - e^{-t/\theta_4^*})$$

where θ_2^* and θ_4^* are the characteristic times of the relaxation, A_1 and A_2 are constants related to the parameter of the model, and $M(t)$ and $M(\infty)$ are the time-dependent and the final mass of the diffusing species respectively. Experimental data[188] for the block copolymer of polystyrene and polybutadiene are described reasonably well by this expression if two time lags are used. The calculated values of $M(t)$ are accurately consistent with the experimental kinetic sorption curves (Fig. 7). The formation of maxima and minima on the kinetic sorption curves was also analysed.[188] It was found that these mass oscillations can be ascribed to standing waves formed in the cylindrical cavity of a McBain balance at some pressures of vapour, the waves being diffuse rather than elastic in nature.

Other measurements of the sorption kinetics of the vapours of various liquids by block copolymers of polystyrene and polybutadiene have also been reported.[188] The equations were found to give an accurate description of the kinetics of the process, and the time lags determined from sorption data agreed reasonably well with the relaxation times obtained in independent stress relaxation experiments.

Relaxation experiments carried out in a medium of the sorbate[188] confirmed the assumption that the penetration of sorbate into the polymer causes degeneracy of the long relaxation times. All these results indicate that the relaxation mechanism associated with the swelling of the polymers is the main determining factor in the sorption process.

A statistical analysis of the behaviour of block copolymers during swelling, allowing for the conformation of the chains connecting the domains, has also been described.[190]

Thus the sorption process, which is accompanied by a large change in volume (i.e. by swelling), is closely bound to the relaxation processes involving conformational rearrangements of the macromolecules. These rearrangements are responsible

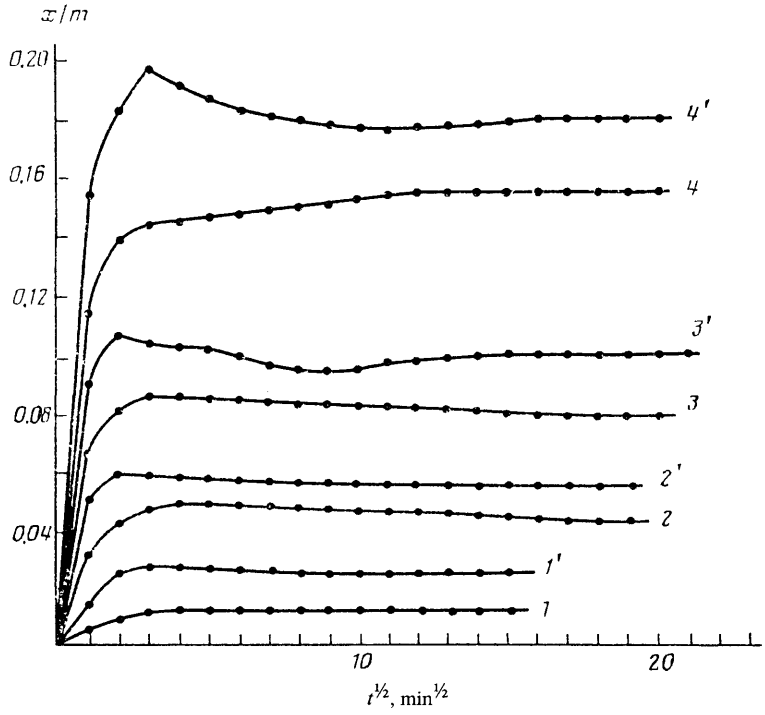


Figure 7. Kinetic curves for the sorption of iso-octane vapour on a block copolymer of polystyrene and polybutadiene containing 30% of polystyrene blocks. The ratio p/p_S is: *1*) and *1'*) 0.2, *2*) and *2'*) 0.4, *3*) and *3'*) 0.6, *4*) and *4'*) 0.8. Numbers without primes and with primes correspond to samples prepared from solution and from dispersion respectively[188] (x/m is the increase in weight of the sample caused by sorption, p/p_S is the relative vapour pressure of the solvent).

for the time-dependence of the diffusion coefficient. Allowing for this time-dependence gives an accurate description of the swelling kinetics and explains many other features of the process.

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Nesmeyanov Element-organic Compounds Institute of the USSR Academy of Sciences, Moscow

Institute of Physical Chemistry of the USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 1407-1420 (1984)

The Use of Lanthanide Shift Reagents in the Analysis of the Micro-structure of Polymers by NMR Spectroscopy

Yu.E.Shapiro

The principal results obtained by using lanthanide shift reagents (LSR) to analyse the micro-structure of polymer chains by ^{1}H and ^{13}C NMR spectroscopy have been examined. A short theoretical introduction to the LSR method has been given, and the magnetic properties of the lanthanides have been examined from the viewpoint of their possible use as LSR. Particular attention has been paid to the solution of the main problems in the structural analysis of polymer chains: the determination of stereoregularity and the nature of the alternation of the monomer units along a copolymer chain, and the investigation of the distribution of *cis*- and *trans*-units and the conformational mobility of homopolymer chains with and without polar groups. The bibliography contains 57 references.

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I. INTRODUCTION. THE MICRO-STRUCTURE OF POLYMERS

The physicochemical properties of a polymer are determined chiefly by the structure of the repeat unit of the chain, but there are practically no ideal regular chains. Real polymers contain the most varied chain structural defects, which can produce significant changes in the properties of the polymer. Information on the distribution of defect units of different types along the chain provides a quantitative reflection of the micro-structure of the polymer.

High-resolution NMR now occupies a dominant position in the study of the micro-structure of polymer chains.[1-4] Because of the marked dependence of the electronic shielding of the nuclei on the chemical environment, the displacement of the signals in the NMR spectra takes place as a consequence of not only the alternation of chemically different monomer units but also the alternation of the relative configurations of successive identical monomer units containing pseudo-asymmetric carbon atoms. This makes it possible to use NMR spectroscopy to solve three types of problem: 1) the composition analysis of the distribution of monomer units along the chain, including the determination of the type of orientational connection "head to head", "head to tail", and "tail to tail"; 2) measurement of the degree of stereoregularity of the chain; and 3) conformational analysis, including the study of phase transformations (of the globule–coil type).

Experimental approaches to the analysis of the micro-structure of the chain are associated with the measurement of the relative concentration of different fragments and the sequence of monomer units from the integral intensities of their signals in the NMR spectrum. The maximum length of this fragment which can be identified by NMR at present does not exceed 8–9 monomer units.[5] Thus the experimental data describe directly the distribution of the units only in short sections of the chain. To analyse the distribution of the units along the entire chain of the macromolecule, it is necessary to assume that the processes controlling the growth of the chain during polymerisation are random in character and are described by Bernoulli or Markov statistics of first and second orders.[4]

The information provided by the NMR spectra of polymers (particularly ^{1}H NMR) is decreased, however, by the fact that the nuclei of aliphatic groups around which there are no electronegative atoms give signals with similar chemical shift values. Moreover, there are a whole range of fundamental physical factors[5] leading to broadening and overlap of the NMR signals from different structural sequences of the polymer chains. Thus the number of polymers which can be readily analysed is small, and to investigate the micro-structure of polymers it is usually necessary to use either shift reagents or NMR spectrometers with a superconducting magnet, or a combination of these methods.

II. LANTHANIDE SHIFT REAGENTS IN NMR SPECTROSCOPY. THEORY OF THE METHOD

The influence of paramagnetism on the characteristics of nuclear resonance was detected by Bloembergen and Dickinson.[6] The characteristic features of NMR in paramagnetic systems have been examined in detail in a large number of theoretical and experimental studies[7-10] and summarised in a number of reviews and monographs.[11-15]

The paramagnetic centres include lanthanide cations having an unpaired electron. The interaction between the unpaired electron and the nucleus whose magnetic resonance is being observed is revealed by an isotropic hyperfine shift of the signal,[7] a change in the nuclear relaxation times T_1 and T_2, and in the nuclear polarisation of the spins as a result of the Overhauser effect.[8] These changes give information on the electronic and geometric structure of the ligands joined to the paramagnetic centres.

1. The Paramagnetic Shift

The isotropic shift of the signals in the NMR spectra of paramagnetic substances is determined by the sum of two types of interaction: contact and pseudocontact.

A Fermi contact shift takes place if the spin density of the unpaired electron is delocalised and is transferred through a system of chemical bonds to the nucleus whose resonance is being observed. A contact shift obeys the Curie law and in the case of a one-spin state with an isotropic g-tensor is described by the equation:[6]

$$\frac{\Delta H}{H_0} = -\frac{Ag^2\beta^2}{g_N\beta_N}\cdot\frac{s(s+1)}{3kT}$$

where A is the hyperfine interaction constant, g_N the nuclear g-factor, β_N the nuclear magneton, H_0 the intensity of the external magnetic field, β the Bohr magneton, g the Landé

factor, k the Boltzmann constant, T the absolute temperature, and s the spin quantum number of the electron.

The contact shift of a signal is observed with the condition that $T_{1e}^{-1} \gg A$, where T_{1e} is the electronic spin–lattice relaxation time. Contact shifts are large for oxygen and nitrogen nuclei coordinated directly to the paramagnetic centre, and also for carbon chemically combined with these atoms. For more distant atoms, including all protons, the contact shifts are small, and the paramagnetic shifts observed in the NMR spectra have pseudocontact character.[11-15]

The pseudocontact shift is determined by the dipole–dipole interaction of the spins of the unpaired electron and the nucleus whose resonance is being observed; its magnitude depends on the electron configuration of the paramagnetic ion, the degree of magnetic anisotropy of the ligand field, and temperature.

The magnitude of the pseudocontact shift of a signal is inversely proportional to the cube of the distance from the paramagnetic centre to the nucleus being observed, and depends on angular factors. For axial symmetry of the complex, the pseudocontact shift is determined[7] by the McConnell–Robertson equation:

$$\frac{\Delta H}{H_0} = -\frac{\beta^2 s(s+1)}{9kT}(g_{\parallel}^2 - g_{\perp}^2)\frac{3\cos^2\theta - 1}{r^3} \qquad (2)$$

where $g_{\parallel}$ and $g_{\perp}$ are the components of the g-tensor of the magnetic anisotropy in directions parallel to and perpendicular to the principal axis of the complex, r the distance to the nucleus, and θ the angle between the radius vector $\boldsymbol{r}$ and the principal axis of the complex.

The dependence of the pseudocontact shift on the geometry of the complex,[7] described by Eqn.(2), makes it possible to assign the signals in the spectrum of a ligand with known structure or to solve the inverse problem, that is from the known assignment to obtain information on the geometry of a molecule.[10-16]

2. Paramagnetic Broadening

In the presence of a paramagnetic centre, broadening of the NMR signals is observed, due to the acceleration of the relaxation of the nuclear spin and the influence of exchange by molecules of the substrate between bound and free states. The main factor determining the width of the NMR signals of the substrate is the electronic spin–lattice relaxation time of the paramagnetic ion T_{1e}. For the complexes of ions with small values of $T_{1e} \ll \hbar/Ag\beta$ (Eu^{3+}, Pr^{3+}, Nd^{3+}), slight broadening is observed. Ions with large $T_{1e} \gg \hbar/Ag\beta$ (Gd^{3+}, d elements such as Mn^{2+}) give extensive broadening.[14]

The spin–lattice T_1 and spin–spin T_2 relaxation times for nuclei with spin 1/2 in the presence of a paramagnetic centre are determined by the Solomon–Bloembergen equations.[8] The first terms of these equations are due to dipole–dipole interaction, and depend on the distance r between the nucleus being observed and the paramagnetic centre. This interaction is determined by the correlation time of the dipole electron–nucleus interaction τ_c. The second terms, which do not depend on r, are characterised by the correlation time of the contact interaction τ_e. The relaxation times are influenced only by variable effects whose correlation times are of the same order of magnitude as the period of the Larmor precession of the nuclear spins.

The correlation times are determined by the expressions

$$\tau_c^{-1} = \tau_R^{-1} + \tau_S^{-1} + \tau_M^{-1} + \tau_D^{-1} \qquad (3)$$

$$\tau_e^{-1} = \tau_S^{-1} + \tau_M^{-1} \qquad (4)$$

where τ_R, τ_S, τ_M, and τ_D are the correlation times corresponding to rotational motion, relaxation of the electron spin, and chemical and diffusion exchange respectively.

3. The Magnetic Properties of the Lanthanides and Their Use as Shift Reagents

Lanthanides have short electronic spin relaxation times $\tau_S \cong 10^{-12}$–10^{-13} s at 300 K. Exceptions are provided by ions with the $4f^7$ electron configuration (Gd^{3+}, Eu^{3+}), which have long times τ_S ($\tau_S \cong 10^{-10}$ s for Gd^{3+}). The unique position of Gd^{3+} among the lanthanides is related to the fact that its ground state is $^8S_{7/2}$, $L = 0$, and the magnitude of the angular momentum is determined entirely by the spin. This state does not interact with an electric field, so that the rate of relaxation of the electron spin decreases.

Thus the lanthanides, except Gd^{3+} and Eu^{3+}, should have little influence on the magnetic resonance line width, if chemical exchange is sufficiently rapid, and they can be used as shift reagents. Gadolinium, like the ions of d elements, is a relaxation (broadening) reagent. The action of Eu^{3+} as a shift reagent is due to the displacement of the ground and excited states.

The theoretical calculation of the magnitude of pseudocontact shifts brought about by the lanthanides has been described.[9]

The correct interpretation of the data obtained using lanthanide shift reagents (LSR) also gives complete pictures of the structure of compounds in solution, which can only be compared with X-ray diffraction data for determining crystal structures. The LSR most widely used as paramagnetic probes are europium and praseodymium salts and their complexes with 2,2,6,6-tetramethylheptan-3,5-dione (dpm), 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctan-4,6-dione (fod), and d-camphor. The salts are used in polar solvents. In most known cases, europium salts displace the signals towards strong fields, and praseodymium salts towards weak fields.[16] In non-polar solvents, complexes with the above ligands, lanthanide tris(β-diketonates), are used, for example $Eu(fod)_3$, $Pr(dpm)_3$; europium β-diketonates usually displace NMR signals in the spectra of substrates towards weak fields, and praseodymium towards strong fields.[17]

NMR spectra obtained in the presence of LSR are interpreted by two methods. The first involves the qualitative analysis of the spectrum modified using LSR. In the second case the shift values are used to obtain information on the structure of the substrate.

The qualitative interpretation of the spectra does not require assumptions about the nature of the bond between the LSR and the substrate. When the LSR is added, the assignment of the signals in the NMR spectrum of the substrate is simplified because of the difference in the induced shift of the signals from different nuclei. It follows from Eqn.(2) that a greater shift is undergone by the signals of nuclei situated closer to the coordination centre of the substrate molecule.

To obtain information on the structure of a substrate from Eqn.(2), it is necessary to have a large amount of data on the structure of the complex. Some of these data can be obtained by X-ray diffraction and from luminescence spectra.[15] This does not however eliminate the difficulties associated with the need to separate from the induced total paramagnetic shift of the signal the pseudo-component, which is determined by the geometry of the substrate.[17]

All methods for separating the contributions of contact and pseudocontact shifts are based on the difference in the dependence of their magnitude on the atomic number of the

lanthanide. The behaviour of the signals in the presence of europium and gadolinium is most informative for investigating the question of the existence of contact shifts in a given system.[12,16] If a shift is detected in the presence of gadolinium, this indicates the existence of a contact shift of the signal from the nucleus of the substrate being considered, since the pseudocontact shift induced by gadolinium is zero. By measuring the displacement of the signals from the same nuclei in the presence of different lanthanides, it is possible to obtain a system of linear equations which make it possible to determine quantitatively the contact and pseudocontact contributions to the induced shifts.[12,15] An unsatisfactory feature of all existing methods of separation is the need to make an assumption about the axial symmetry of the complex.[15]

III. THE USE OF LANTHANIDE SHIFT REAGENTS TO ANALYSE THE MICRO-STRUCTURE OF A POLYMER CHAIN

1. The Separation of Signals from Stereosequences

The first applications of LSR to study a number of polymers with functional groups were aimed merely at simplifying the form of the NMR spectra.[18-29] The addition of $Eu(dpm)_3$, $Eu(fod)_3$, and $Pr(fod)_3$ improved the resolution of the signals in the spectra of polymethyl methacrylate (PMMA), polyvinyl methyl ether, polyvinyl ethyl ether, polyvinyl acetate, polypropylene oxide, polysiloxane,[18,19] polyesters,[20,21] polyols,[22-26] polylacetones,[27,28] polypeptides,[29] and other polymers.

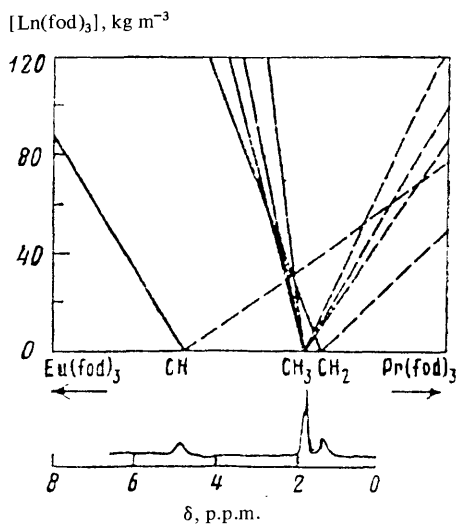


Figure 1. Influence of the concentration of $Eu(fod)_3$ (continuous lines) and $Pr(fod)_3$ (broken lines) on the ^1H NMR spectrum of polyvinyl acetate solution.[18]

Guillet and co-workers[19] were the first to discover that the shifts of the triad signals from the methyl and methoxycarbonyl groups of PMMA in o-dichlorobenzene decrease in the following order when an LSR is added (*i*-, *h*-, and *s*- denotes iso-, hetero-, and syndiotactic triads): $s\text{-}CCH_3 > i\text{-}CCH_3 > h\text{-}CCH_3 > i\text{-}OCH_3 > s\text{-}OCH_3 > h\text{-}OCH_3$. The order of change in the shifts is different in benzene: $i\text{-}CCH_3 > h\text{-}CCH_3 > s\text{-}CCH_3 > i\text{-}OCH_3 > h\text{-}OCH_3 > s\text{-}OCH_3$. This difference reflects the dependence of the conformation of the polymer on the micro-tacticity.[18-20]

Fig.1 shows the ^1H NMR spectrum of polyvinyl acetate in $CDCl_3$ and the influence of the addition of small quantities of $Eu(fod)_3$ and $Pr(fod)_3$ to the solution.[18] Both reagents separate the signal from the methoxycarbonyl proton into iso-, hetero-, and syndiotactic triads. The slopes of the straight lines on the diagram characterise the relative magnitude of the induced shift. $Pr(fod)_3$ produces larger shifts than $Eu(fod)_3$, and slightly greater paramagnetic broadening.

The determination of the micro-tacticity of poly-β-substituted β-propiolactones is a fundamental problem in the study of stereoregulation. A promising route to its solution has appeared with the use of $Eu(dpm)_3$ to separate the signals from meso (*m*) and racemic (*r*) diads in the ^{13}C NMR spectra.[27] The stereospecificity of induced paramagnetic shifts is due to the difference of 1–4° in the values of the angles θ in Eqn.(2) for the neighbouring carbon atoms of ^{13}CO and $^{13}CH_2$ in the *m* and *r* configurations of the polymer chain as a consequence of the restricted rotation relative to the bond joining these atoms.

The influence of $Eu(dpm)_3$ and $Dy(fod)_3$ on the ^{15}N NMR spectra of polypeptides has been studied.[29] The spectra of Z–Glu–Leu–*Leu–OMe (Fig.2) show that the addition of $Dy(fod)_3$ produces a selective shift of the ^{15}NH signals from different aminoacids. This is due to the difference in the chemical and spatial environments of the nitrogen atoms.

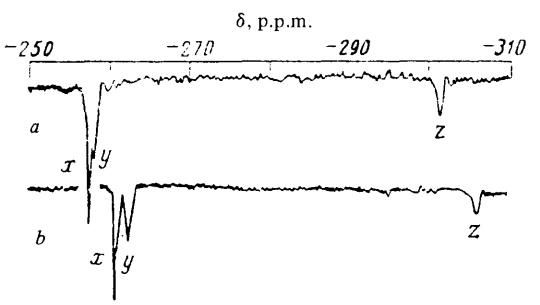


Figure 2. ^{15}N $\{^1H\}$ NMR spectra of a solution of Z–Glu–Leu–*Leu–OMe in CH_2Cl_2 before (*a*) and after (*b*) the addition of $Dy(fod)_3$ in the ratio N/Dy = 60 : 1. The chemical shifts are measured from the signal of $^{15}NO_3$ [29] (*x*—*Leu, *y*—Leu, *z*—Glu).[29]

The paramagnetic shift values depend on the distribution of the europium ions between different coordination centres in polyethylene glycol and polyformaldehyde chains.[22] It should be noted, however, that few authors take account of this distribution, which is capable of influencing the interpretation of the spectra considerably, particularly in the determination of the transformation of the polymer chain.

2. The Conformational Mobility of Homopolymer Chains

All approaches to the examination of the conformation of polymer chains are based on the use of some form of the McConnell–Robertson equation (2) after separation of the

contact and pseudocontact contributions to the induced paramagnetic shift. It is therefore of interest to examine the stereospecific contact interaction in the NMR spectra of polyol–lanthanide complexes (La^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}, Yb^{3+}).[26] If the chain has a planar zigzag conformation, the main contribution to the paramagnetic shift is made by contact interaction. In other cases, the isotropic shift of the signal is predominantly pseudocontact. This was used[30] to establish the possible conformations of iso- and syndiotactic PMMA in solution by comparing the observed values of the pseudocontact shift with the values of the geometric factor $(1-3\cos^2\theta)/r^3$ in Eqn.(2), calculated for all planar or spiral conformations of the chain.

Fig.3 gives the dependence of the values of the induced paramagnetic shifts $\Delta\delta$ of the signals from the protons of three groups (α-CH_3, CH_2, and OCH_3) for iso- and syndiotactic PMMA in solutions in $CDCl_3$ and C_6D_6 on the $Eu(dpm)_3$ concentration. The values of $\Delta\delta$ depend on the distance of the protons from the coordination site, and for syndiotactic PMMA also on the nature of the solvent.

In spite of the fact that a flexible polymer chain cannot have a fixed conformation in solution,[4] it has been shown that isotactic PMMA exists in a right-hand spiral (10/1) conformation. The *trans*-zigzag conformation established for syndiotactic PMMA is a unique case of planar or spiral conformation.

The influence of the shift reagents $Eu(dpm)_3$ and $Pr(dpm)_3$ on the ^1H NMR spectra of a solution of atactic poly-4-vinylpyridine (P-4-VP) in $CDCl_3$ has been studied in the temperature range 28–100 °C.[31] The micro-structure of radical P-4-VP, determined from the ^1H and ^{13}C spectra, corresponds effectively to Bernoulli statistics with $P_m = 0.52$. The shifts of the proton signals in the spectra of the polymer, induced by adding $Eu(dpm)_3$, are due to pseudocontact interaction. The values of the geometric factor were calculated for fragments of the macromolecule with regular iso- or syndiotactic-sequences. The conformations of the polymer were determined from the maximum probability of agreement between the experimental and calculated values of the induced shifts. The concentrations of the structures $[2_1]$ = 47 mole % (TTGG), $[Z_S]$ = 28 mole % (*trans*-zigzag), and $[3_1]$ = 25 mole % (isotactic) agree with the proposed model of the micro-tacticity of P-4-VP. The temperature dependence of the shifts of the ^1H signals indicated a change in the ratio of the conformations of P-4-VP towards an increase in the concentration of the syndio-*trans*-form.

$Eu(fod)_3$ was used similarly to determine the concentration of the TGT conformation of the sequence COCCOC in polyethylene glycol.[25] When europium is added to the polymer solution, the NMR signals assigned to the ethylene protons in the polymer segments separate into four groups of signals from the ethylene protons, close to the end of the chain, and a singlet in a weak field from TGT. The concentration of the TGT form increases rapidly with increase in the number-average molecular mass of the polymer.

3. Analysis of the Nature of the Alternation of Monomer Units Along the Polymer Chain

The use of LSR makes it possible to obtain extensive information on the distribution of the monomer units along copolymer chains, not obtainable by other methods of physicochemical analysis.[32] A necessary condition for the applicability of shift reagents to the analysis of the micro-structure of copolymers, as in the case of homopolymers, is the presence of atoms with an unshared pair of electrons (nitrogen or oxygen) in the main or side chains. The copolymers studied with a nitrogen atom in the side chain include copolymers of acrylonitrile with 1,3-dialkenes,[33–37] and with an oxygen atom, the copolymers of methyl methacrylate (MMA)[38–40] and α,β-unsaturated ketones with 1,3-dialkenes,[41–43] of methyl methacrylate with styrene,[44] and of ethylene with vinyl acetate.[45] In spite of the complexity of the interpretation of the spectra, the LSR method has been applied successfully to copolycondensed polymers containing an oxygen atom in the main chain.[46,49]

The application of the LSR method to copolymers containing a hetero-atom in the side chain is based on the fact that the signals of the triads having a large number of coordination centres, for example CN or CO, and hence a large number of polar (P) monomer units undergo a larger induced lanthanide shift than triads containing chiefly non-polar (N) units. The magnitude of the induced paramagnetic shift of the signals from the triads increases in the series NPN < NPP < PPP, NNN ≪ NNP < PNP.[32–34] This was used to assign the signals in the spectra, and the results agreed well with the results obtained by ^{13}C NMR spectroscopy[47] and with existing statistical theories describing the nature of the growth of the polymer chain.[37–42]

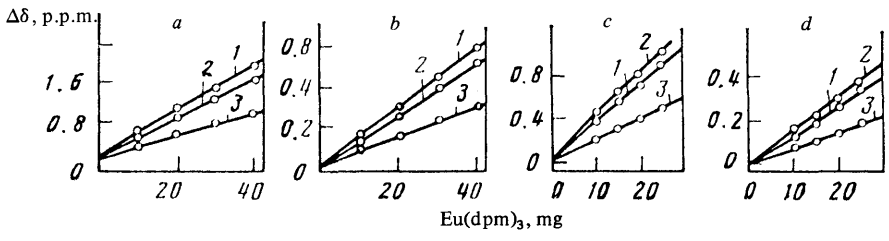


Figure 3. Dependence of the induced paramagnetic shift of the signals of CH_2 (*1*), CH_3 (*2*), and OCH_3 (*3*) on the quantity of $Eu(fod)_3$ for iso- (*a*,*c*) and syndiotactic (*b*,*d*) PMMA at 25 °C (*a*,*b*) and 80 °C (*c*,*d*) in $CDCl_3$.[30]

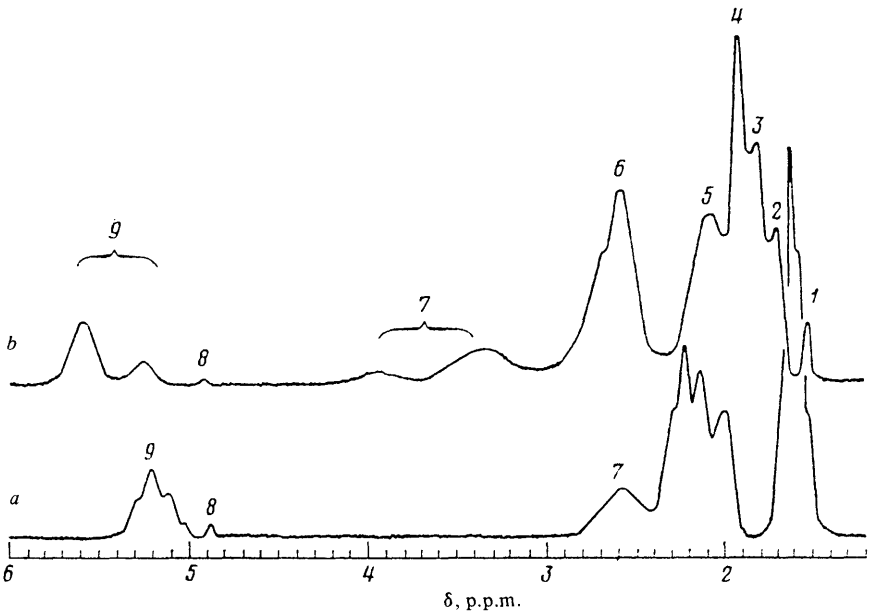


Figure 4. ^{1}H NMR spectra of a solution of the copolymer of isoprene (I) and acrylonitrile (A) (51.2 mole % A) in $CDCl_3$: *a*) without the addition of Eu(fod)$_3$, *b*) after the addition of Eu(fod)$_3$ at a mass ratio Eu(fod)$_3$:copolymer of 1:1. Assignment of the signals: *1*) CH_3-III; *2*) CH_3-AII, CH_2-III; *3*) CH_2-IAI; *4*) CH_3-AIA; *5*) CH_2-AII; *6*) CH_2-AIA + AAI + AAA; *7*) CH–CN; *8*) 1,2-I; *9*) =CH-III + AII + AIA.[35]

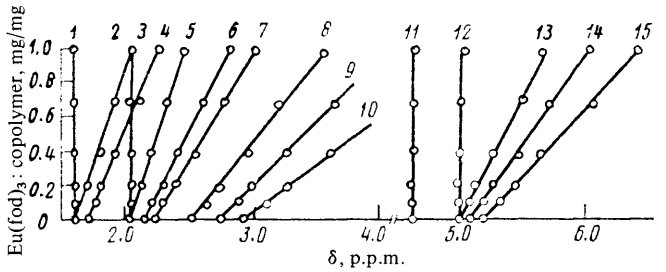


Figure 5. Dependence of the magnitude of the induced paramagnetic shift of the ^{1}H NMR signals of the triad and tetrads in the spectrum of the copolymer of isoprene with acrylonitrile (40 mole % A) on the mass ratio Eu(fod)$_3$: copolymer. CH_3: *1*) III, *2*) IIA; CH_2: *3*) IIA, *4*) IAI, *5*) IAAI, *6*) IAAA, *7*) AAAA; CH, A: *8*) IAI, *9*) IAA, *10*) AAA, *11*) 1,2-I; $=CH_2$, =CH: *12*) III, *13*) AII, *14*) AIA, *15*) AAIA.[36]

Fig.4 gives the ^{1}H NMR spectra of the copolymer of isoprene (I) with acetonitrile (A) before and after the addition of Eu(fod)$_3$. Fig.4*b* shows that after the addition of Eu(fod)$_3$ to the copolymer solution, the signals from different triads containing acetonitrile units are separated and displaced to weaker fields. Fig.5 gives the dependence of the magnitude of the induced paramagnetic shift on the ration Eu(fod)$_3$:copolymer for the signals of the copolymer of isoprene with acetonitrile. The magnitude of the induced shift of the signals increases in the series IAI < IAA < AAA; III ≪ IIA < AIA; CH_3 < CH_2-I ≤ =CH < CH_2-A < CHCN.[36,37] The last series proves that the nitrogen of the nitro-group [cyano group, (Ed. of Translation)] is coordinated to europium.

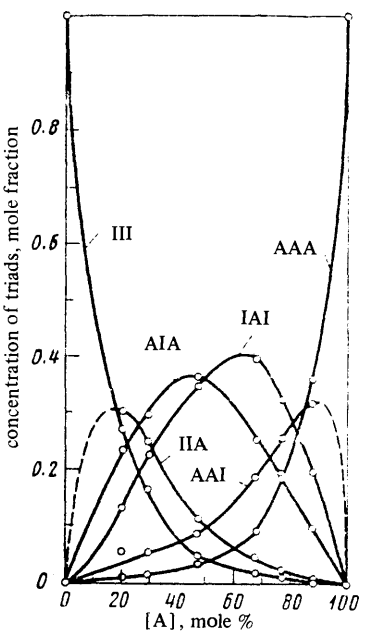


Figure 6. Dependence of the triad composition of copolymers in the mass of isoprene with acrylonitrile on the acrylonitrile concentration.[32]

The values of the integral intensities of the signals from different triads give information on the micro-structure, and make it possible to find the statistics of the distribution of

the monomer units along the chain. Fig.6 gives the dependence of the triad composition of the copolymers of isoprene with acetonitrile, obtained by copolymerisation in the mass, on the acetonitrile concentration [A]. The asymmetry of the arrangement of the maxima on the curves indicates that the nature of the growth of the copolymer chain does not correspond to Bernoulii statistics and that there are mutually opposed tendencies in the formation of the chain by the monomer units: isoprene tends to undergo homopolymerisation, and acetonitrile to undergo heteropolymerisation.[33]

The micro-structure of industrial SKN-18, -26, -40 butadiene–nitrile rubbers with different acetonitrile concentrations was studied analogously.[34] The absence of shift, induced by the addition of $Eu(fod)_3$, of the signal from the 1,2-structures of butadiene and separation into its components made it impossible to reach conclusions about the isolation of the 1,2-structures within the butadiene micro-blocks.

The micro-structure of copolymers of MMA with 1,3-dialkenes has been analysed using a shift reagent.[38–40] $Pr(fod)_3$ was used to determine the micro-structure of copolymers of MMA with isoprene.[38] The growth of the chains of the copolymers obtained in the mass obeys first-order Markov statistics with copolymerisation constants $r_{MMA} = 0.26$ and $r_I = 0.625$.

First-order Markov statistics also describe the copolymer of chlorophene with MMA, since the concentration in it of the pentad with an MMA unit at the centre, determined from the splitting of the methoxyl signal when $Eu(dpm)_3$ is added, agrees with that calculated from the copolymerisation constants.[39]

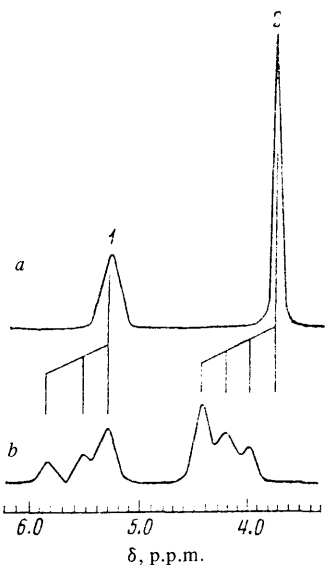


Figure 7. ^1H NMR spectra of a solution of the copolymer of butadiene with MMA in CCl_4: *a*) without the addition of $Eu(fod)_3$, *b*) after the addition of $Eu(fod)_3$; *1*) CH= (MBM, BBM, BBB), *2*) OCH_3 (MMM, MMB, BMB). The signals from the triads were recalculated in the direction of increase in the field.[40]

Fig.7 shows the ranges of the signals from the alkene and methoxyl protons of the copolymer of butadiene (B) with MMA (M).[40] When $Eu(fod)_3$ is added to a solution of the copolymer, these signals are split into the signals from the triad. The magnitude of the induced paramagnetic shift of the signals increases in the series BBB ≪ BBM < MBM; BMB < BMM < MMM; $-CH_2-B <$ =CH– < $-CH_2-M <$ $-OCH_3 <$ CCH_3. The values of the induced shifts indicate that the carboxyl and ester oxygen atoms are coordinated to europium.

The information on the micro-structure of copolymers, obtained by NMR spectroscopy using shift reagents, makes it possible to reach conclusions about the mechanism and topochemistry of the copolymerisation. For example, the dependence of the micro-structure of emulsion copolymers of isoprene with acetonitrile and of butadiene with MMA on the stability of the layer of surface-active agent (SAA) on the surface of the polymer–monomer particle has been established.[32,33,35–37,40] Fig.8 clearly shows the relationship between the criterion of the stability of the layer of SAA (the half-width $\Delta\nu_{1/2}$) of the signal from $(CH_2)_n$ in the ^1H NMR spectrum of mixed micelles of sodium alkylsulphonate (SAS) with potassium dresinate (PDR)[48] and the triad composition of the copolymers obtained in these systems.[35,37] The chain growth of the emulsion copolymers of isoprene with acetonitrile is described by first-order Markov statistics.[35]

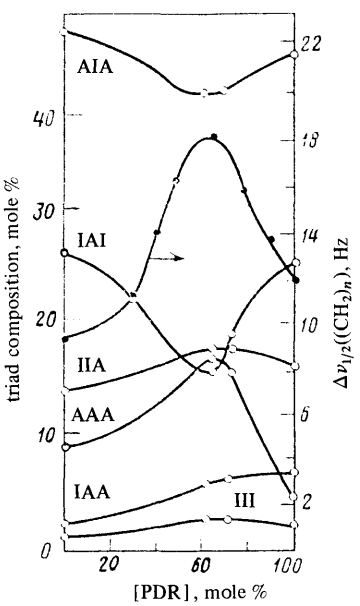


Figure 8. Dependence of the concentration of the triads and $\Delta\nu_{1/2}((CH_2)_n)$ in the ^1H NMR spectra of micelles of SAS and PDR on the PDR concentration.[37]

Analogous results on the influence of the stability of the SAA layer on the micro-structure have been obtained for emulsion copolymers of butadiene with MMA.[40] The SAA used were salts of aliphatic acids, differing in methylene chain length or in the number and position of double bonds, and hence in the stability of the SAA layer on the surface of the polymer–monomer particle. In particular, increase in the length of the methylene chain leads to an increase in the packing density and stability of the SAA layer.[40] Fig.9 shows that the dependence of the concentration of block and alternant triads in the copolymers on the length of the methylene chain is linear. The growth of the chain of the

emulsion copolymers of butadiene with MMA obeys first-order Markov statistics. The results made it possible to distinguish the zones in which homopolymerisation of monomers of different polarity takes place.[35,36,40]

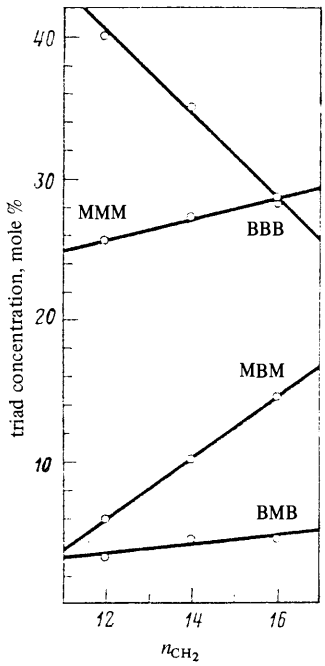


Figure 9. Dependence of the concentration of the triads in the emulsion copolymer of butadiene with MMA on the number of methylene groups in the molecules of the saturated aliphatic acid emulsifiers.[40]

The shift reagent $Eu(fod)_3$ has also been used to analyse the micro-structure of copolymers of α,β-unsaturated ketones (K) with isoprene (I), obtained by radical copolymerisation in the mass and in solution.[41-43] When $Eu(fod)_3$ was added, the signal from the alkene protons was separated into three components, which were assigned to the triads III, IIK, and KIK (listed in the direction of decrease in the field).[41] The experimental values of the concentrations of the triads show good agreement with those calculated from the ^{13}C NMR spectra and from the values of the copolymerisation constants, determined independently (by copolymerisation directly in the NMR spectrometer). The high concentration of the triad KIK confirms the tendency for the copolymers studied to show alternation.[42]

The addition of $Eu(fod)_3$ to a solution of the copolymer of methyl methacrylate with styrene leads to an increase in the resolution in the spectrum of the signals from triad configurations giving a contribution to the signal from the OCH_3 group.[44] The orientation of the LSR molecule in the copolymer chain is determined by the steric influence of the aromatic ring.

The ^1H NMR spectra of copolymers of ethylene with vinyl acetate have been interpreted using $Eu(fod)_3$.[45] The displaced signals from the methine and methyl acetate protons were assigned to the triad sequences of vinyl acetate, and their concentration was compared with that calculated from Bernoulli's model. Comparison of the results showed good agreement.

^1H NMR spectroscopy using $Eu(fod)_3$ and $Pr(fod)_3$ as LSR has been used to analyse the distribution of monomers in the chains of copolyarylates based on dimethyl-bis-phenol, phenolphthalein, and terephthalyl chloride, obtained by high-temperature polycondensation in α-chloronaphthalene.[46] The coefficients of the non-regularity of the copolyarylate chain were determined from the splitting, in the presence of the shift reagent, of the signal at 8.40 p.p.m. from terephthalyl chloride into peaks from the triad. In the copolyarylate synthesised at the isokinetic temperature (200 °C) for the given system, the copolymer units are distributed along the chain according to a random law, whereas in the copolyarylates obtained at other temperatures, copolymer blocks tend to form.

The use of LSR gives a good effect in ^{13}C NMR spectroscopy, as shown by an analysis of the distribution of sequences from the "unreliable", in the sense of the assignment of the signals, spectra of the homo- and copolymers of 1,3,5-trioxane and 1,3,5-trioxepane with 1,3-dioxolane.[49]

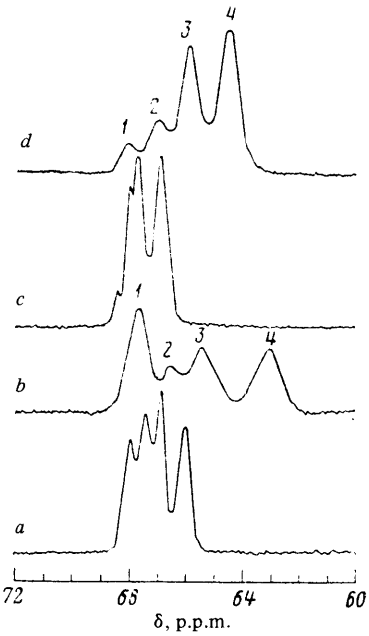


Figure 10. ^{13}C $\{^1H\}$ NMR spectra of the methine carbons of the VA units of a VC–VA copolymer (55 mole % VA) (*a*,*b*) and of the VP units of a VC–VP copolymer (70 mole % VP) (*c*,*d*) before (*a*,*c*) and after (*b*,*d*) the addition of $Pr(fod)_3$ in the ratio $Pr(fod)_3$:copolymer = 0.5. Solvent C_6D_6, temperature 50 °C. Assignment of the signals: *1*) VC–VA(VP)–VC, *2*) VC–VA(VP)–VA(VP), *3*) iso-VA(VP)–VA(VP)–VA(VP), and *4*) stable homotriads.[50]

In any case, the use of LSR in ^{13}C NMR spectroscopy improves the resolution of the signals, for example, $Pr(fod)_3$ has been used[50] to separate the methine signals of copolymers of vinyl chloride (VC) with vinyl acetate (VA) and vinyl propionate (VP). The ^{13}C NMR spectra (Fig.10) show that

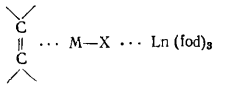
when $Pr(fod)_3$ is added, the methine signal separates into four peaks, corresponding to different triad configurations.

An approach analogous to that described for copolymers has been used to study the distribution of epoxide groups in epoxy-*cis*-polybutadiene and epoxy-*cis*- and epoxy-*trans*-polypentene polymers with different degrees of epoxidation by ^1H [51] and ^{13}C [52] NMR spectroscopy. When $Eu(fod)_3$ was added to the polymer solution, the signals from the $-CH_2-\underset{O}{C}-C$, $-CH_2-C=C-$, and $-CH=CH-$ groups separate into signals from the triad sequences of the epoxidised (E) and non-epoxidised (N) units. The magnitude of the induced paramagnetic shifts of the signals increases in the series: NNN $\ll$ NNE < ENE; NEN < NEE < EEE; $-CH=CH-$ < $-CH_2-C=C-$ < $-CH_2-\underset{O}{C}-\underset{O}{C}-$ $\leqslant -CH-\underset{O}{CH}-$. The calculation showed that the distribution of the epoxide units in the epoxypolyalkenylenes obeys Bernoulli statistics.

4. The Distribution of *cis*- and *trans*-Units in Polymers Not Containing Polar Groups

The shift reagent method has been widely used to analyse the micro-structure of polymers and copolymers containing units with polar groups. This method, however, can give useful information on the micro-structure of polymer chains containing double bands, but without polar groups. One of the methods of "depositing" the lanthanide on the polymer is by the selective chemical modification of the polymer chain, for example by epoxidation. It should be noted, however, that selective chemical modification involves considerable difficulty.

A recent paper[53] proposed the use, for alkenes, of lanthanide shift reagents combined with Ag, Pd, and Rh salts, which are capable of forming π-complexes with alkenes and complexes with lanthanides of the type:



where M is a metal atom, and X a group capable of coordinating to a lanthanide.

It has been shown possible[54,55] to "deposit $Eu(fod)_3$ on π-complexes of the double bonds of a polymer chain with $AgNO_3$. This method, based on the established[56] difference in the stability constants of the π-complexes of silver with *cis*- and *trans*-alkenes, makes it possible to distinguish *cis*- (C) and *trans*- (T) isomers, and also the diads CC, CT(TC), and TT without deuteriation and spin–spin decoupling for any working frequencies of the ^1H NMR spectrometer.

Fig.11 gives the ^1H NMR spectra of polybutadiene solutions before and after the addition of the $AgNO_3$–$Eu(fod)_3$ system. After the addition of the shift reagent, the signals from the methylene and alkene protons of polybutadiene are split into two (*cis*- and *trans*-) and three (CC, CT(TC), TT) components. The magnitude of the induced paramagnetic shift increases linearly as far as a mass ratio $Eu(fod)_3$: polybutadiene = 3 : 1, after which the relationship reaches a plateau, since possible coordination sites on the polymer molecule are exhausted.

Thus the use of LSR to analyse the micro-structure of macromolecular compounds and to investigate the mechanism of the polymerisation of those polymers in whose NMR spectra the signals from monomer or stereo-sequences are not resolved, is extremely effective. The determination of the

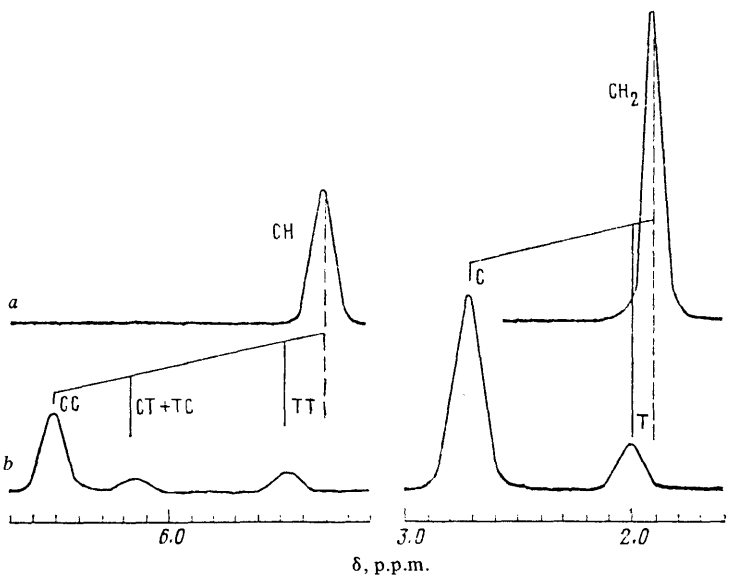


Figure 11. ^1H NMR spectra of a solution of polybutadiene in $CDCl_3$ before (*a*) and after (*b*) the addition of $AgNO_3$–$Eu(fod)_3$.[55]

correspondence of the chain growth to a particular statistic makes it possible to detect the influence of fine effects of intermolecular association[57] on the mechanism of polymerisation.

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Yaroslavl' Polytechnical
Institute

Russian Chemical Reviews

September 1984

Translated from *Uspekhi Khimii*, 53, 1425-1462 (1984)

U.D.C. 541.118 : 546.02 : 549.3/7

The High-temperature Microcalorimetry of Inorganic Substances

N.D.Topor and Yu.L.Suponitskii

The essential features of high-temperature microcalorimetry have been described, and the possibilities provided by its use in various fields such as inorganic chemistry, mineralogy, power engineering, etc. have been demonstrated. The procedures of high-temperature microcalorimetry have been classified according to the types of process studied: solution, oxidation, hydrogenation, dissociation, phase transformations, the mixing of melts, etc., and illustrated for substances with different compositions and uses: metals, oxides, salts, synthetic and natural compounds, and minerals. The results of the studies have been compared with data obtained by calorimetry involving solution in aqueous solutions and by combustion calorimetry. The bibliography contains 423 references.

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I. INTRODUCTION

Heat-conducting calorimeters,[1] the theory and practice of which were developed by Tian[2] and Calvet,[3-9] have been called microcalorimeters, because of their high sensitivity in the measurement of the heats of various reactions and physical transformations. The name indicates that it is possible to measure very small quantities of heat (microcalories) using specimens with different masses and dimensions. Microcalorimeters are usually classified as instruments for low (90–500 K), medium (273–700 K), and high (273 to 2100 K) temperatures. The present review deals chiefly with microcalorimeters for high temperatures (273–1800 K), and the possibilities provided by their use in chemistry, mineralogy, the production of ceramics, metallurgy, and other fields. The types of microcalorimeter indicated do not differ fundamentally from one another. The main differences are in the construction of the working thermostats (blocks), where the detector cells surrounded by the thermojunctions are placed; in the materials from which they are made; and also in the construction of the apparatus for initiating the reactions. The heat losess from a high-temperature calorimter increase in proportion to T^4; in practice, this means that the loss of heat at 1000 K will be eight times greater,

and that at 1500 K 27 times greater, than that at 500 K. The fact that it is impossible to eliminate these losses makes it difficult to use more accurate adiabatic and other calorimeters at high temperatures (1050–1600 K).[10,11]

The design of high-temperature microcalorimeters (HTMC) makes it possible, instead of eliminating the heat losses from the working cells, to achieve their practically complete compensation during the experiment. Thus in spite of the lower accuracy of the measurements compared with the above-mentioned calorimeters, HTMC have the advantages of simplicity, convenience in use, and reliability of the measurements in long experiments at high temperatures (1000–1800 K). A high-temperature microcalorimeter is a universal heat-measuring instrument, which can be used to determine the enthalpies of various chemical reactions, physical transformations, and phase transformations (fusion, volatilisation, adsorption, mixing of solutions, polymorphic transformations, order–disorder transformations, etc.). Compared with other calorimeters, HTMC make it possible to study heterogeneous reactions and not only to determine the quantity of heat liberated or absorbed but also simultaneously to study the kinetics of the process. These and a number of other advantages have led to the extensive application of high-temperature microcalorimetry in chemistry,[12–16] mineralogy,[17–22] metallurgy,[23–30], the study of the thermodynamics of solid solutions (order–disorder transformations),[31,32] etc. HTMC are now also used to study the thermochemistry of salt and metallic systems used to accumulate solar energy and ground heat.[33–36]

II. ESSENTIAL FEATURES OF THE METHOD AND APPARATUS

High-temperature microcalorimeters (1300 K) appeared in 1955–1966[37–39] after the development of the theory of heat-conducting calorimeters[40–42] and the construction of electronic regulators for maintaining high temperatures in the block with a high accuracy.[43–45] The design of the Setaram Calvet high-temperature microcalorimeter (1000 °C) is shown in Fig. 1. The actual microcalorimeter consists of two calorimeter cells placed symmetrically in cylindrical holes in a massive block made of stainless steel[46] or fused alumina.[47] A battery of Pt–PtRh (13%) thermocouples (396 junctions) is placed between the outer surface of each detector cell and the cylindrical surface of the hole in the block. The batteries of the two cells are connected according to a differential scheme. Some of the thermocouples can be used to generate the Peltier effect in the detector cells.[4,48,49]

A slight change in the temperature of the block produces identical heat fluxes to the two cells, and identical EMF's are produced in the thermo-batteries, and as a result of the differential connection they compensate one another. A change in temperature in one of the cells produces an EMF which is proportional to the intensity of the heat flux from this detector cell to the block (or conversely). This EMF is amplified and recorded graphically using a recorder. The area bounded by the heat-liberation curve and the zero line, which is proportional to the heat of the process being studied, is measured using planimeters, electronic integrators, or computers.[50,51] The form of the curve defines the thermal power of the process at each moment of time, so that its kinetics can be studied.[52–54] The instrument is calibrated to determine its basic constants, that is its sensitivity and time constant.[4,8] The geometric form of the specimen and the degree of filling of the cell influence the nature of the curve, and may introduce errors into the time constant of the instrument.[55,56]

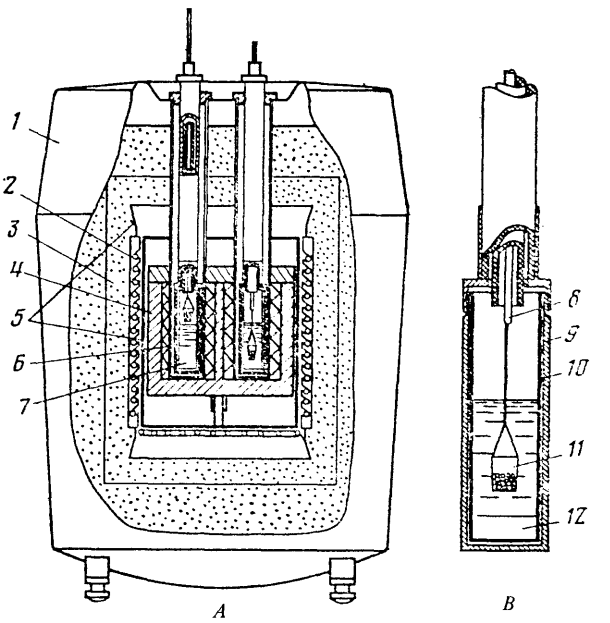


Figure 1. *A*) Calvet microcalorimeter; *1*) calorimeter casing, *2*) heater, *3*) furnace, *4*) massive block, *5*) metal screens, *6*) thermocouples, *7*) calorimetric cell; *B*) calorimetric cell: *8*) ceramic rod, *9*) metal cell casing, *10*) platinum beaker, *11*) platinum crucible, *12*) solvent melt.

The constants of the microcalorimeter are determined experimentally by various methods: by electrical calibration from the Joule effect, by placing an ohmic resistance in the detector cell;[57] by measuring the known heats of fusion or solution of standard chemical compounds;[25,58,59] from the known heats of chemical reactions;[60–64] and by mixing† standard substances for which the temperature changes in enthalpy are known. The calibration using the Joule effect can also be carried out without an ohmic resistance, by using the resistance of the thermocouples surrounding the detector cell (Peltier effect); when calibration from the Peltier effect is used, there is no heat flux along the leads.[49,65] Electrical calibration from the Joule effect has not been widely used in high-temperature microcalorimetry. HTMC are mainly calibrated by mixing, that is the basic constants of the instrument are determined from the change in the heat content of standard specimens of Pt, Au, or Al_2O_3, which after being brought to constant temperature at 298 K are dropped into the working cell of the microcalorimeter, heated to the required temperature.[66,67] The mixing method is used to calibrate calorimeters which are to be used to measure high-temperature enthalpies or to measure the enthalpies of solution of metals and compounds in various solvent melts. In a number of procedures, additional apparatus is introduced into the cells, for example to initiate chemical reaction. The possibility of introducing various pieces of equipment into the working cells (ampoules, manipulators, initiating assemblies, stirrers) represents the main advantage of HTMC over the other types of calorimeter.

† Other terms are encountered in the literature: the dump method, drop calorimetry.

Methods involving the programming and complete automation of the calorimetric experiment have been widely used in recent years.[68-70]

Large high-temperature microcalorimeters. Extensive development of high-temperature microcalorimetry took place after the foundation, in 1957, of the Institut de Microcalorimetrie et de Thermogenese de Marseille,[71] in whose workshops the first high-temperature microcalorimeters (1300 K) were constructed;[46] using their pattern, the firm of Setaram in Lyons began the mass production of instruments with the following technical characteristics: temperature range 300–1300 K, heating rate 0.5–60 K h^{-1}, sensitivity 2.5 mJ mW^{-1} or 4 μV mW^{-1}, time constant 120–130 s (1100 K); dimensions of the working cells: diameter 17 mm, height 80 mm, volume 15 cm^3; parameters of the HTMC: height 100 cm, diameter 60 cm, mass 300 kg. This HTMC (1300 K) belongs to the class of large microcalorimeters, and as a result of its temperature stability under isothermal conditions it can be used to carry out long experiments (weeks or months). Large high-temperature microcalorimeters (1300 K) have been used mainly to study the thermochemistry of metals and metallic alloys.[40,55,72-75] Assemblies making it possible to carry out experiments in air or in an inert medium and in a vacuum, depending on the aims of the study of solid–liquid metallic systems, have been developed.[74-86]

To increase the sensitivity and improve the reproducibility of the results in the measurement of the heat content and the determination of the heat capacity of solids, a special working cell was used,[19] with a partition and a semi-automatic device for dropping the specimen into the cell.[87,88] A simple procedure for determining the heats of fusion and solution involves dropping the solid specimen (298 K) into the liquid situated in the working cell of the calorimeter at the given temperature[27,28,88] (Fig. 2*a*). A disadvantage of this method is that the thermal effect of the process being recorded consists of two effects: an endothermic effect due to the change in the enthalpy of the solid substance, and the thermal effect of the solution of the solid in the liquid. The two effects are superimposed on one another, and their separation in the integration of the areas under the curves is difficult and leads to large errors, which are difficult to take into account.[17] Much better results in the determination of heats of solution are obtained when the solid is suspended in a small dish at a short distance from the liquid, and dropped into the liquid after temperature equilibrium has been reached, for example by opening a clamping mechanism, controlled from outside the apparatus (Fig. 2*b*).[80] Very reliable and accurate results are obtained by the "indirect drop" procedure. The solid specimen, at room temperature, is dropped into a graphite ampoule situated above the melt, and brought to the same temperature as the melt in the calorimeter (Fig. 2*c*). When temperature equilibrium has been reached, the solid specimen is lowered by means of a manipulator into the liquid for the measurement of the enthalpy of solution. The procedure can be carried out in a vacuum and in an inert atmosphere.

In the study of the enthalpies of mixing of molten salts, one of the salts in a sealed quartz ampoule is lowered into the working cell containing a melt of the other salt. When temperature equilibrium has been reached, the ampoule is broken by a manipulator, and the enthalpy of mixing of the melts or the solution of the solid salt in the melt is measured (Fig. 2*d*).[89-92] To determine the enthalpies of solution of small specimens, a special device to start the reaction was constructed for use with Setaram HTMC.[71] To prevent corrosion, the device was made of a ceramic oxide (Al_2O_3) and a heat resistant alloy which did not form a scale up to 1600 K. The successful microcalorimetric study of metals and alloys led to the development, in various laboratores, of specieal HTMC (1500 K and 1880 K) for studying the partial enthalpies of the reaction of oxygen with non-stoichiometric oxides of iron, uranium, zirconium, etc. In these instruments, as a result of the intensive radiative transfer of heat, direct contact between the thermocouples and the wall of the cell or block is not necessary. The calibration is carried out from the known enthalpies of oxidation of thorium by oxygen.[93-98] HTMC (1000 K) with graphite or platinum cells in which it is possible to carry out experiments in a vacuum have been constructed to study the enthalpies of solution of metals in liquid aluminium and tin[99,100] and to measure the enthalpies of mixing of liquid metals with sulphur and selenium.[101]

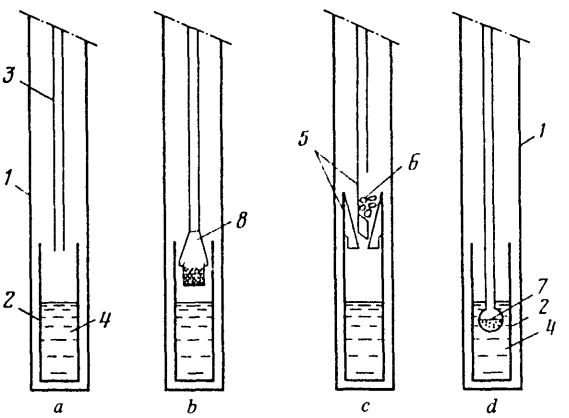


Figure 2. Types of reaction assembly placed in the calorimeter to measure the enthalpies of solution in melts: *1*) cell casing, *2*) platinum reaction vessel, *3*) directing tube, *4*) solvent melt, *5*) graphite specimen holder for heating to the temperature of the solvent and for dropping it, *6*) specimen, *7*) ampoule containing the specimen, *8*) holding clamp for heating the specimen to the temperature of the solvent and for dropping it.

In 1955, Kleppa (USA) constructed a high-temperature heat-conducting microcalorimeter with one working cell, designed for the study of the solution of metals at 800 K,[37] and in the period 1960–1966 he developed HTMC with two working cells,[12,38,102,103] designed for the study of the solution of oxides and silicates in oxide melts, selected for the first time for these purposes in another study.[104] In a subsequent model, the Chromel/Alumel thermojunctions were replaced by Pt–PtRh (13%) thermojunctions, and the HTMC were calibrated by mixing using platinum and gold specimens. Kleppa was the first to use an original device for initiating solution, placed symmetrically in both cells. An HTMC operating up to 1100 K with a quartz device for "starting" the reaction was constructed[105] for determining the enthalpies of solution of solid inorganic compounds in melts with the composition $3Na_2O.4MoO_3$ by Navrotsky's method.

High-temperature microcalorimeters with a small number of thermocouples. Heat-conducting calorimeters with a limiting working temperature of up to 1800 K have recently been developed. The blocks of these calorimeters are made of molybdenum and have smaller dimensions; some workers[106,107]

have used planar PtRh (6%)–PtRh (30%) or WRh (5%)–WRh (10%) thermo-batteries with a smaller number of thermocouples, placed in an aperture in the side of the working cell. This HTMC is designed to operate in air and in a vacuum at 800–1800 K.[108,109] Another type of calorimeter, manufactured by Setaram, differs from the HTMC (1300 K) produced by the same firm in that both calorimeter cells of fused Al_2O_3 are arranged in it vertically and coaxially one above the other (Fig.3). The detector cells, the thermobattery, and the device for circulating argon and for cooling with water are placed in a vertical heater with a large uniform temperature zone; the temperature of the heater can be raised to 2000 K. The procedure for carrying out measurements with this apparatus in the study of metals and metallic systems has been described,[110–113] but its possibilities have not been fully studied. In the next type of heat-conducting microcalorimeter, in contrast to the Tian–Calvet microcalorimeter, the junctions of the thermo-batteries were connected in series.[114,115] This HTMC can operate in the temperature range 298–1500 K or 103–900 K under programmed heating conditions in a vacuum or in a medium of inert gases. A heat-conducting microcalorimeter of spherical shape, in which the liquid components, in a sealed quartz ampoule, are mixed by rotating the calorimeter through 180° has been constructed for determining the heats of mixing of volatile, solid, and liquid salts. The HTMC is calibrated from the Joule effect using a calibration resistance, and the uncertainty of the determination of the enthalpies of mixing is 4%.[116]

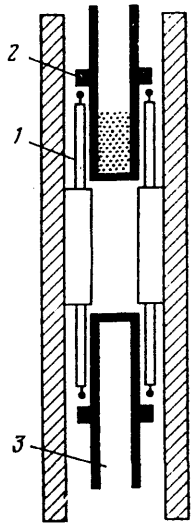


Figure 3. Diagram of the vertical arrangement of the cells in the HTMC (1800 K): *1*) thermocouple, *2*) reaction assembly with the melt, *3*) empty cell.

Heat-conducting calorimeters of the DTA type. Heat-conducting microcalorimeters fitted with a temperature controller for maintaining a stable rate of heating (or cooling) while preserving the advantages of HTMC are acquiring the additional functions of instruments for quantitative thermal analysis. It is difficult, however, to carry out experiments under programmed heating conditions using large HTMC (1300 K) with a large number of thermojunctions, with a large time constant. The heating rate should be low (0.5 to 8 K h^{-1}), or stability of the zero line is not achieved. The long time required to carry out the experiment, and the need to decrease the senstivity of the instrument, make large HTMC unsuitable for experiments under constant heating conditions, although the possibility does exist (for determining large thermal effects, for example on fusion).[39,64,90,95,117,118]

In the USSR, one of the first microcalorimeters for studying the rates of heterogeneous solid–gas reactions and dissociation at 770 K was constructed in the Chemistry Department of Moscow State University.[119] A microcalorimeter designed for the study of heat capacities, phase transformations, the ageing of metals, etc., operating at 400–1100 K, has been described[120]. A differential microcalorimeter, constructed[121] in accordance with the Calvet principle and operating in the range 300–1000 K, is designed mainly for quantitative thermal analysis; it is calibrated electrically, has an accuracy of 3–5%, and the mass of the specimen is 0.6–6 g.

Microcalorimeters designed to operate under conditions of heating and cooling (1–20 K min^{-1}) are called "scanning calorimeters". The Setaram differential scanning microcalorimeter (DSC) combines the accuracy and sensitivity of the traditional HTMC with the speed of carrying out the experiments characteristic of DTA.[122,123] This DSC operates in the range 150–1000 K under isothermal and scanning conditions; the operation of the instrument is controlled by a computer, and the time constant of the detector is 12 s.

III. ENTHALPIES OF SOLUTION OF INORGANIC COMPOUNDS

In many calorimetric procedures, enthalpies of solution provide a basis for determining enthalpies of formation, which are fundamental thermochemical characteristics used in chemistry, mineralogy, metallurgy, power engineering, etc.[124–135] Various refractory compounds and minerals are insoluble in acids, however, even at high temperatures (298–353 K). The calorimetric study of solution in aqueous solutions of acids is therefore unsuitable for determinining the enthalpies of formation of refractory compounds or minerals. A much more effective method than acid calorimetry is provided by high-temperature solution microcalorimetry, where a liquid melt, having considerable solvent power at 1000–1200 K, is used instead of an aqueous acid solution. The procedure for carrying out the measurements was developed in 1960 [38] after the development of a high-temperature Tian–Calvet microcalorimeter with a special quartz device for studying the solution of specimens with a mass of 50–300 mg.[12,37] This procedure is used to determine the enthalpy change in the solution of a weighed specimen of a solid in a liquid solvent consisting of a melt with a definite composition.

A similar device for solution, made of a refractory ceramic and a heat-resistant alloy, has been described.[66] An advantage of this device is that it is possible to work with small specimens of the substances being studied, so that rare materials can be investigated (toxins, synthetic compounds, cosmic minerals). The enthalpies of solution in melts are generally about one tenth of the enthalpies of solution in aqueous acid solutions. This means that although the uncertainty of the determination of the enthalpy of solution in HTMC is ~1%,[18,52,136] whereas that for calorimetry involving solution in acids is ~0.1%, the uncertainty of the enthalpy of formation of a substance being studied will be the same in both cases (Table 1). The main advantage of the HMTC method for studying solution is that it is possible to measure the enthalpies of solution of refractory compounds

(oxides, chromites, ferrites, silicates, aluminosilicates, etc.) using specimens with a mass of 5–30 mg. A limitation of the method must be mentioned, however, namely the difficulty of studying hydrated compounds, including natural and synthetic minerals. Procedures for studying solution in melts have been examined in detail.[9,12,17,18,51,66,136–141]

Table 1. Comparative characteristics of calorimetric methods for determining the enthalpies of formation of silicates.[20,53]

Characteristics of the method	Calorimetry involving solution in acids (HF etc.)	High-temperature microcalorimetry involving solution in melts
Principle of the method	adiabatic calorimeter	Calvet microcalorimeter
Working temperature range, K	289–398 (depending on the type of calorimeter)	298–1800 (depending on the type of calorimeter)
Mass of specimen for one experiment	500–2000 mg	5–300 mg
Example of an experimentally determined quantity: $(\Delta H^0_T)_{solution(\alpha\text{-}SiO_2)}$, kcal mole^{-1}	−33.0±0.02	−1.01±0.05
Uncertainty of the determination (attainable) of $(\Delta H^0_T)_{solution}$, %	0.1	1
Uncertainty of the calculated enthalpy of formation of the silicate (ΔH^0_f), kcal mole^{-1}	0.1–0.2	0.1–0.2
Influence of dilution and change in the concentration of the solution on the value of ΔH^0_T, solution	considerable	slight
Solubility of the most important oxides (Al_2O_3, Cr_2O_3, MgO, SiO_2, etc.)	satisfactory or poor	good (at 1000–1300 K)
Work with hydrated compounds	possible	difficult

1. Oxide Solvents

As in classical solution calorimetry,[142] the main problem in the thermochemical study of the solution of substances in melts is the choice of the solvent melt. Up to the present, in spite of the accumulation of knowledge on the physical chemistry of melts and the equilibrium diagrams obtained, there is no scientifically based criterion for selecting a solvent melt in relation to the composition of the compounds being studied. The main requirements which must be satisfied in the choice of a solvent can be formulated as follows.

1. With allowance for the existing temperature limit of the measurements in the high-temperature microcalorimetric procedure, the melting point of the solvent should be comparatively low (900–1200 K), and the vapour pressure should be so low that the enthalpy of volatilisation does not distort the measurements being made.

2. The solvent should have a buffer capacity, that is it should have a concentration range in which the enthalpy of solution is practically independent of the composition of the solvent.

3. The solvent should be stable in the atmosphere in which the measurements are being made.

The most important characteristic of the solvent melt is its acid–base behaviour; the magnitude and sign of the enthalpy of solution are determined by the degree of acidic or basic character of the solvent.[12] The scale of basic strength of oxide solvent melts can be interpreted as a series of states of the oxygen ion between O^{2-} and O^- as a result of polarisation in the presence of metal cations.[143] The equilibrium for the acid–base behaviour in an oxide melt can then be written in the form:

$$\text{acid} + O^{2-} \rightarrow \text{base}$$

The greater the activity of the oxygen ion, the greater the basic strength of the melt.[144–146] For example, in the Na_2O–MoO_3 system, sodium oxide is a strongly basic oxide (base), and MoO_3 is a strongly acidic oxide (acid). Thus the solution of MoO_3 in melt rich in sodium oxide can be represented as the following chain of equilibria:

$$O^{2-}(\text{liquid}) + MoO_3(\text{crystalline}) \rightarrow MoO_4^{2-}(\text{liquid})$$
$$MoO_4^{2-}(\text{liquid}) + MoO_3(\text{crystalline}) \rightarrow Mo_2O_7^{2-}(\text{liquid})$$
$$MoO_3(\text{crystalline}) \rightarrow MoO_3(\text{liquid})$$

Solvents based on oxides, so-called oxide solvents, have been most widely used in high-temperature microcalorimetry. The possibility of using an oxide solvent (V_2O_5) to dissolve the oxides of a number of metals at 958 ± 5 K and lead vanadates at 953 K was first demonstrated by Yokokawa and Kleppa.[147,148] V_2O_5 was not used in other studies, since it does not show acid–base properties. The efforts of research workers were subsequently directed to the search for melts combining acidic and basic properties, since only these melts can fulfil the functions of a calorimetric solvent and give an acid–base equilibrium. The equilibrium diagram of the PbO–B_2O_3 system[149–151] showed a range of compositions (17–67% B_2O_3) existing in the liquid state at 973 K; a buffer capacity was detected for the composition $2PbO.B_2O_3$, and this was found to be suitable for dissolving many oxides (SiO_2, GeO_2, Fe_2O_3).[152] A less widely used melt for these oxides has the composition $9PbO.3CdO.4B_2O_3$, from the ternary PbO–CdO–B_2O_3 system.[153,154]

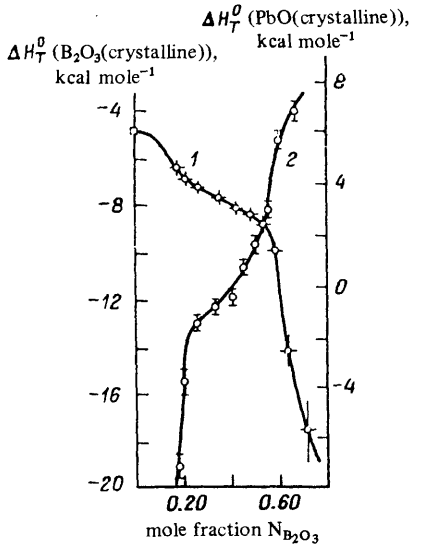


Figure 4. Dependence of the enthalpy of solution of PbO (*1*) and B_2O_3 (*2*) on the mole fraction of B_2O_3 in a PbO–B_2O_3 melt at 1173 K; *N* is the mole fraction.

The composition ranges of the PbO–B_2O_3 system corresponding to a buffer capacity of the solvent can be seen from Fig. 4, but oxides such as TiO_2, SnO_2, NiO, and their compounds are insoluble in these solvents. A so-called molybdate melt with the composition $3Na_2O.4MoO_3$ (75% Na_2MoO_4–25% MoO_3) (Fig. 5) has been proposed for these oxides;[155] because of its appreciable volatility, this melt is unsuitable at temperatures above 700 °C, and is unstable in

a reducing medium. A study of the acid–base properties of the K_2MoO_4–MoO_3 system[156] established that in the composition range 35–80 mole % MoO_3, this system has a lower melting point than Na_2MoO_4–MoO_3, and compositions with 40–50 mole % MoO_3 can be used as a calorimetric solvent at 820 K (Fig. 6).

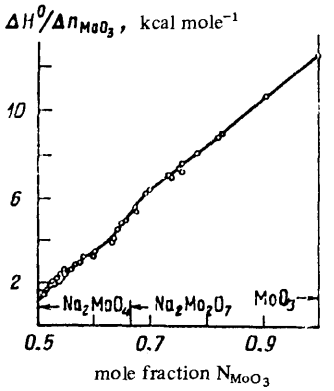


Figure 5. Dependence of the enthalpy of solution of MoO_3 on the mole fraction of MoO_3 (N_{MoO_3}) in an Na_2O–MoO_3 melt.

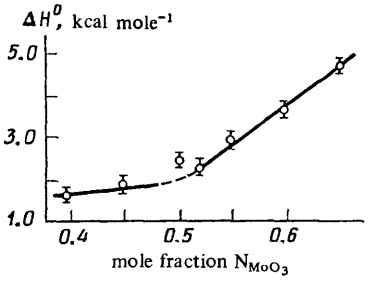


Figure 6. Dependence of the enthalpy of solution of MoO_3 on the mole fraction (N) of MoO_3 in a K_2O–MoO_3 melt.

To find new calorimetric solvents, the following oxide systems have been studied: PbO–SiO_2 at 1173 K,[157] PbO–GeO_2 at 1173 K,[158] Li_2O–B_2O_3 at 1213 K, and Na_2O–B_2O_3 at 1258 K.[159] A solvent with the composition 0.5 $LiBO_2$–0.5 $NaBO_2$, liquid at 940 K, was detected.[159] The ternary eutectic mixture with the composition Na_2O–B_2O_3–SiO_2, liquid at 1973 K, is a good solvent for dissolving SiO_2, Al_2O_3, MgO, CaO, FeO, and MnO in a reducing medium. This composition is hygroscopic, however, and this introduces a number of difficulties in its preparation and storage. Buffer properties have been detected for various compositions of the Na_2O–P_2O_5 system.[160] In the range 56–61 mole % Na_2O, the phosphates are liquid at 1116 K, and are of undoubted interest as promising calorimetric solvents. Up to the present, however, the phosphate melt has not found extensive application in high-temperature microcalorimetry. The main characteristics of the widely used and new solvent melts are summarised in Table 2. The practically unlimited possibilities in the further search for solvent melts are opening up extensive opportunities for using high-temperature microcalorimetry to study various classes of inorganic substance.

Table 2. Compositions and ranges of application of solvent melts used in high-temperature solution microcalorimetry.[17,20,249]

Composition of melt	Range of application K	Used to dissolve	Notes
$2PbO·B_2O_3$ or $9PbO·3CdO·4B_2O_3$ *	920–1170	SiO_2, GeO_2, Fe_2O_3, Cr_2O_3, MgO, CaO, NiO, CuO, ZnO, CdO, Cu_2O	not suitable for dissolving TiO_2, SnO_2, Mn_2O_3
$3Na_2O·4MoO_3$	870–1020	TiO_2, SnO_2, Mn_2O_3, MgO, CaO, NiO, ZnO, CdO Ln_2O_3	acidic oxides and SiO_2 do not dissolve well; volatile at T > 970 K
$0.35Na_2O·0.35B_2O_3·0.3SiO_2$	1070–1170	SiO_2, Al_2O_3, MgO, CaO, FeO **, MnO **	hygroscopic (special storage conditions)
$0.5Li_2O·0.5Na_2O·B_2O_3$ ($LiBO_2$+$NaBO_2$)	940	WO_3, FeO, MnO	new solvent, procedures not developed
$2.5Na_2O·1.5P_2O_5$ ($NaPO_3$+$Na_4P_2O_7$)	1120	WO_3	ditto

*Solvent with narrower range of application.
**A reducing medium is required.

2. Minerals and Silicate Systems

The enthalpies of formation of minerals are used for thermodynamic calculations when modelling the processes involved in natural and synthetic mineral formation.[161,162] High-temperature solution microcalorimetry has been developed for refractory natural and synthetic minerals.

Al_2O_3–SiO_2 system. The enthalpy of solution of the oxide Al_2O_3 was determined for the first time in 1964,[153,163] after which the enthalpies of solution of polymorphic forms of the compound Al_2SiO_5—the minerals andalusite, kyanite, sillimanite and mullite—in the ternary solvent $9PbO.3CdO.4B_2O_3$ at 968 ± 2 K was determined.[164,165] The calculated enthalpies of formation and other thermochemical constants (entropy, heat capacity) were used to construct the p–T diagram of the Al_2O_3–SiO_2 system over a wide range of temperatures and pressures.[166] Additional studies of the enthalpies of solution of minerals with the composition Al_2SiO_5 in molten $2PbO.B_2O_3$ at 974 + 2 K [167,168,169] made it possible to refine the p–T diagram, so that the coordinates of the triple point of the Al_2O_3–SiO_2 system coincided with published data.[170–173]

The measured enthalpies of solution of different forms of SiO_2 (quartz, cristobalite, coesite, stishovite, glass) in moltent $9PbO.3CdO.4B_2O_3$ at 970 ± 2 K, and the high-temperature enthalpies determined by mixing, were used to construct the p–T diagram giving the stability of the coesite–stishovite system, to calculate the thermodynamics of the polymorphic transformation[86] and the high-temperature equilibria for the forms of SiO_2, and to reach conclusions important for geology and seismology.[174] For sillimanite it was established that there is a difference in the enthalpies of solution of specimens[175] kept at different temperatures before the experiments (influence of the degree of ordering of the structure).

MgO–Al_2O_3–SiO_2 system. The stability fields of the solid phases in the MgO–Al_2O_3–SiO_2 system are usually studied using apparatus for high and superhigh pressures and temperatures.[176,177] The technical difficulties and the time

required for this experimental method, and the lack of published thermochemical data for the thermodynamic analysis of the stability fields of the solid phases on the $p-T$ diagrams, led to the development of the thermochemical study of the minerals in molten $2PbO.B_2O_3$ at 1000–1300 K [178–181] (Tables 3 and 4). The enthalpies of formation and heat capacities calculated in this way, and the known entropy values, can be used to carry out calculations for many reactions which are models for processes taking place in the earth's crust and upper mantle and used in silicate technology. The differences observed in the enthalpies of solution of natural compounds and their synthetic analogues indicate that the data obtained for a synthetic system cannot be transferred uncritically to a natural system, even when the compositions of the phases are similar.

Table 3. Enthalpies of solution of oxides in high-temperature solvents based on boric oxide (ΔH_T^0, kcal mole^{-1}).

Oxide	T, K	ΔH_T^0	Refs.	T, K	ΔH_T^0	Refs.
	$9PbO\cdot3CdO\cdot4B_2O_3$			$2PbO\cdot B_2O_3$		
α-Al_2O_3	978	7.6±0.2	[153]	965	7.88±0.24	[180]
α-Al_2O_3	—	—	—	1173	7.47±0.13	[180]
α-Al_2O_3	—	—	—	970	7.73±0.08	[179]
β-Al_2O_3	978	2.3	[164]	—	—	—
δ-Al_2O_3	978	5±3	[164]	—	—	—
Al_2O_3	978	4.6	[164]	—	—	—
SiO_2	943	−3.64±0.07[a]	[165]	943	−1.02±0.05	[197,404]
SiO_2	970	−3.1±0.1[b]	[86]	965	−1.04±0.07[a]	[180]
SiO_2	970	−2.8±0.1[c]	[86]	1173	1.03±0.05[a]	[180]
SiO_2	970	−3.5±0.1[d]	[86]	970	−1.23±0.07[a]	[179]
SiO_2	970	−3.8±0.1[e]	[86]	986	−0.76±0.10[a]	[205]
SiO_2	970	−3.5±0.1[f]	[86]	973	−1.01±0.05[a]	[185]
SiO_2	970	−4.45±0.15[g]	[86]	1070	0.19±0.05[a]	[185]
SiO_2	970	−4.5±0.1[i]	[86]	—	—	—
MgO	965	−2.19±0.16	[197]	965	0.72±0.03[h]	[180]
MgO	970	−2.19±0.16	[222]	1173	2.01±0.54[h]	[180]
MgO	970	−8.86±0.07[j]	[222]	1173	1.99±0.11[h]	[185]
MgO	958	−9.4±0.6[k]	[147]	970	1.18±0.08[h]	[179]
MgO	—	—	—	986	1.39±0.17[h]	[205]
MgO	—	—	—	1070	1.68±0.23[h]	[185]
MgO	—	—	—	1170	2.1±0.4[h]	[185]
MgO	—	—	—	955	−1.8±0.8	[197]
CaO	958	−32.7±0.7[k]	[147]	936	−13.05±0.22	[205]
CaO	—	—	—	970	−13.18±0.39	[137]
CaO	—	—	—	973	−13.30±0.07	[185]
CaO	—	—	—	967	−15.08±0.17	[187]

Notes: [a] quartz; [b] quartz; [c] quartz-2; [d] cristobalite; [e] coesite-1; [f] coesite-2; [g] stishovite; [h] periclase; [i] vitreous; [j] solvent $3Na_2O.4MoO_3$; [k] solvent V_2O_5.

Measurement of the enthalpies of solution of magnesium silicates and aluminates in molten $2PbO.B_2O_3$ at 973 K [180] and $MgAl_2O_4$ in $9PbO.3CdO.4B_2O_3$ [181,182] showed that the solution of MgO takes place slowly and is not quantitative at 973 K, and is characterised by two thermal effects: a large exothermic effect is first observed, followed by a small endothermic effect. This two-stage solution was attributed[181] to the formation of an intermediate compound (exothermic effect), followed by its solution (endothermic effect). At 1173 K the solution of MgO is complete and takes place at a high rate, and the exothermic effect almost disappears; [183–186] the results of the determination of the enthalpy of formation of magnesium silicate show good agreement with the data obtained by calorimetry involving solution in acids (see Table 11 below). Thus the study of magnesium

Table 4. Enthalpies of solution [$(\Delta H_T^0)_{solution}$, kcal mole^{-1}] of silicates in molten $2PbO.B_2O_3$ and enthalpies of formation from the oxides (ΔH_f^0, kcal mole^{-1}); the number of experiments is given in brackets.

Compound	T, K	$(\Delta H_T^0)_{solution}$	$-\Delta H_f^0$	Refs.
Al_2SiO_5 (sillimanite)	974	6.93±0.01 (8)	—	[167]
Al_2SiO_5 Isillimanite)	963	7.11±0.29 (11)	—	[175]
Al_2SiO_5 (sillimanite)	970	6.92±0.09 (11)	0.57±0.14	[179]
Al_2SiO_5 (sillimanite-II)	970	7.07±0.09 (11)	—	[179]
Al_2SiO_5 (kyanite)	974	8.35±0.17 (15)	—	[167]
Al_2SiO_5 (kyanite)	973	8.38±0.23 (6)	—	[193]
Al_2SiO_5 (kyanite)	973	8.42±0.11 (12)	—	[397]
Al_2SiO_5 (andalusite)	973	8.01±0.30 (3)	—	[193]
Al_2SiO_5 (andalusite)	973	7.42±0.15 (10)	—	[397]
Al_2SiO_5 (andalusite-I)	974	7.55±0.19 (10)	0.71±0.30	[168]
Al_2SiO_5 (andalusite-II)	974	7.62±0.21 (24)	—	[168]
$Mg_2Al_4Si_5O_{18}$ (cordierite)	963	28.1±1.5 (8)	16.1±0.7	[181]
$Mg_2Al_4Si_5O_{18}$ (cordierite, vitreous)	963	25.9±1.3 (5)	—	[181]
$Mg_2Al_4Si_5O_{18}$ (cordierite)	967	30.04±0.86 (6)	—	[178]
$Mg_2Al_4Si_5O_{18}$ (cordierite)	970	27.54±0.22 (8)	15.87±0.31	[179]
$Mg_2Al_4Si_5O_{18}$ (cordierite, synthetic 1.0% FeO)	970	27.95±0.42 (6)	16.28±0.48	[179]
$MgSiO_3$ (enstatite)	967	8.95±0.33 (7)	—	[177]
$MgSiO_3$ (enstatite)	967	8.4±1.9 (1)	—	[180]
$MgSiO_3$ (enstatite)	970	8.78±0.13 (24)	8.81±0.17	[179]
$Mg_{0.9}Al_{0.2}Si_{0.9}O_3$ (enstatite)	970	7.74±0.11 (9)	7.01±0.15	[179]
$MgSiO_3$ (enstatite)	965	8.36±0.19 (13)	8.68±0.21	[180]
$MgSiO_3$ (enstatite)	1173	11.19±0.15 (7)	8.15±0.57	[180]
$Mg_2Si_2O_6$ (enstatite)	970	17.20±0.21 (5)	—	[198]
$MgSiO_3$ (clinoenstatite)	1170	18.28±0.19 (12)	8.36±0.27	[187]
$Al_2SiO_4F_2$ (topaz, fluoride)	970	—	21.96±0.85	[407]
$Mg_2Al_4SiO_{10}$ (sapphirine)	967	21.78±3.15 (6)	48.95±3.23	[128]
$Mg_2Al_4SiO_{10}$ (sapphirine, 1.7% FeO)	970	20.02±1.22 (12)	45.88±1.25	[179]
Mg_2SiO_4 (forsterite)	970	16.11±0.24 (23)	14.97±0.27	[179]
Mg_2SiO_4 (forsterite)	965	15.84±0.13 (7)	15.44±0.05	[180]
Mg_2SiO_4 (forsterite)	1173	19.91±0.33 (6)	14.88±0.83	[180]
Mg_2SiO_4 (forsterite)	1170	19.22±0.19	14.30±0.33	[184]
$Mg_3Al_2Si_3O_{12}$ (pyrope, synthetic)	970	27.79±0.32 (18)	20.21±0.38	[137]
$Mg_3Al_2Si_3O_{12}$ (pyrope)	970	27.73±0.28 (5)	—	[199]
$Mg_3Al_2Si_3O_{12}$ (pyrope)	973	16.7±6 (7)	—	[191,192]
$Ca_3Al_2Si_3O_{12}$ (grossular)	973	42.5±5 (8)	—	[191,192]
$Ca_3Al_2Si_3O_{12}$ (grossular)	970	42.2±0.4 (7)	—	[199]
$Ca_3Al_2Si_3O_{12}$ (grossular)	970	42.41±0.4 (11)	77.91±0.6	[137]
$Ca_3Fe_2Si_3O_{12}$ (andradite-I)	975	51.1 (6)	—	[191,192]
$Ca_3Fe_2Si_3O_{12}$ (andradite-II)	975	51.6 (3)	—	[191,192]
$Ca_2Al_2SiO_7$ (gehlenite)	970	—	30.64±0.31	[395]
$CaMgSi_2O_6$ (diopside)	970	20.53±0.75 (17)	—	[199]
$CaAl_2SiO_6$ (oligoclase)	970	11.5±0.2 (9)	—	[199]
$CaAl_2SiO_6$ (oligoclase)	970	11.55±0.23	18.23±0.29	[137]
$Ca_2MgSi_2O_7$ (akermanite)	970	—	42.92±0.72	[395]
$CaMgSi_2O_6$ (diopside, synthetic)	970	20.38±0.21 (6)	—	[198]
$CaMgSi_2O_6$ (diopside)	970	20.53±0.25 (17)	34.99±0.41	[137]
$CaMgSi_2O_6$ (diopside)	975	20.38±0.37 (10)	—	[184,185]
$MgCaSi_2O_6$ (diopside, vitreous)	1170	23.46±0.34 (8)	33.35±0.47	[184,185]
$MgCaSi_2O_6$ (diopside, natural)	986	20.95±0.25 (13)	34.3±0.4	[205]
$MgCaSi_2O_6$ (diopside, synthetic)	986	20.82±0.28 (8)	—	[205]
$MgCaSi_2O_6$ (diopside)	986	20.90±0.26 (21)	—	[205]
$MgCaSi_2O_6$ (diopside, vitreous)	986	0.111±0.085 (7)	—	[205]
$CaSiO_3$ (wollastonite, synthetic)	970	7.01±0.22 (5)	—	[137]
$CaSiO_3$ (wollastonite, synthetic homogeneous)	970	7.07±0.20 (14)	21.48±0.36	[137]
$CaSiO_3$ (wollastonite, high-pressure phase)	970	5.43±0.15 (5)	19.84±0.34	[137]
$NaAlSi_3O_8$ (albite)	970	5.23±0.23	—	[208]
$KAlSi_3O_8$ (orthoclase)	970	10.06±0.58	—	[208]
$CaSiO_3$ (pseudo-wollastonite)	970	5.51±0.06 (7)	19.92±0.31	[137]
$CaSiO_3$ (wollastonite)	973	6.96±0.29 (8)	21.48±0.39	[184]
$CaSiO_3$ (wollastonite-I)	1170	9.13±0.31 (8)	—	[184]
$CaSiO_3$ (wollastonite-II)	1070	7.76±0.73	—	[184]
$CaSiO_3$ (pseudo-wollastonite)	973	5.70±0.10 (12)	—	[184]
$CaAl_2SiO_8$ (anorthite, synthetic)	970	15.2±0.3 (38)	23.14±0.45	[137]
$CaAl_2SiO_8$ (anorthite, natural)	970	16.02±0.36 (16)	23.93±0.48	[137]
$CoCaSi_2O_6$	986	17.51±0.33 (10)	26.7±0.5	[205]
$NiCaSi_2O_6$	986	21.08±0.33 (9)	27.0±0.5	[205]
Mn_2SiO_4	986	14.20±0.20 (4)	12.2±0.3	[205]
$MnSiO_3$ (rhodonite)	986	6.98±0.26 (6)	6.3±0.3	[205]
$MnSiO_3$ (pyroxyoptite)	986	6.92±0.19 (6)	—	[205]
$MnSiO_3$ (rhodonite)	986	6.95±0.22 (12)	—	[205]
Ni_2SiO_4 (olivine structure)	986	19.86±0.93 (5)	—	[254]
Ni_2SiO_4 (spinel)	986	18.43±0.57 (7)	—	[254]
α-Co_2SiO_4	986	15.49±0.17 (7)	—	[206]
β-Co_2SiO_4	986	13.34±0.35 (4)	—	[206]
γ-Co_2SiO_4	986	12.80±0.25 (3)	—	[206]
$CoSiO_3$	986	6.92±0.23 (5)	—	[206]
α-Fe_2SiO_4	986	3.74±0.13 (6)	—	[206]
γ-Fe_2SiO_4	986	3.04±0.15 (4)	—	[206]
$FeSiO_3$	986	13.70±0.07 (5)	—	[206]
$MgAl_2O_4$ (spinel, synthetic)	970	14.29±0.14 (5)	5.38±0.18	[199]
$MgAl_2O_4$ (spinel)	965	14.51±0.51 (19)	5.93±0.56	[180]
$MgAl_2O_4$ (spinel)	960	14.81±0.37 (6)	5.33±0.67	[180]
Al_2SiO_5[a] (sillimanite)	968	5.47±0.01 (7)	—	[166]
Al_2SiO_5[a] (andalusite)	968	5.95±0.10 (4)	—	[166]
Al_2SiO_5[a] (kyanite)	968	6.33	—	[165]
Al_2SiO_5[a] (mullite)	968	10.08±0.10 (5)	—	[166]
$MgAl_2O_4$[b]	970	14.13±0.22	8.72±0.29	[222,182]

Notes. [a] solvent $9PbO.3CdO.4B_2O_3$; [b] solvent $3Na_2O.4MoO_3$.

compounds in melts must be carried out at temperatures not lower than 1173 K.[136,187] Measurement of the enthalpies of solution of sapphirine in $2PbO.B_2O_3$ at 973 K showed the influence of temperature on the stability of natural ordered and synthetic disordered sapphirines.[188,189]

$CaO-MgO-Al_2O_3-SiO_2$ system. The enthalpies of formation of the solid phases of this system, determined from the enthalpies of solution in molten $2PbO.B_2O_3$ at 970 K, have been determined[137,190] (see Tables 4 and 5). The dependence of the values obtained for the enthalpy of solution on the size of the anorthite specimen was determined;[155] no significant change in the enthalpies of solution was observed for specimens weighing 43.72–34.90 mg. The enthalpy of solution of natural garnets (grossular, andradite, and pyrope) in molten $2PbO.B_2O_3$ at 973 K has been determined experimentally.[191] The phase relationships for pyrope and minerals of granulite and eclogite facies have been examined by the Schreinemakers method on coordinates $p-T$.[192,193] The thermochemical data for grossular $Ca_3Al_2(SiO_4)_3$, andradite $Ca_3Fe_2(SiO_4)_3$, and uvarovite $Ca_3Cr_2(SiO_4)_3$ have been analysed, and the most reliable experimental data on the $p-T$ equilibria have been used to calculate the Gibbs free energy.[194]

The thermochemical properties of the most important phases of the $CaO-MgO-SiO_2$ system have also been studied[195] by high-temperature solution microcalorimetry in molten $2PbO.B_2O_3$ at 1000–1300 K,[183,184] and the properties of $MgSiO_3$ have been studied at 965 ± 2 K in two solvents: $2PbO.B_2O_3$ and $9PbO.3CdO.4B_2O_3$ (Table 4).

New data on the enthalpy of the $\alpha \rightarrow \beta$ phase transformation of $CaSiO_3$ have been obtained from the enthalpies of solution of the two phases in molten $2PbO.B_2O_3$ at 973 K.[196] Improvements in the experimental technique for high-temperature solution microcalorimetry[137,198,199] made it possible to increase the accuracy of the determination of the enthalpies of solution of the phases and solid solutions of the $CaO-MgO-SiO_2-Al_2O_3$ system. Thus for a number of minerals of this system, synthesised at high temperatures and pressures, the enthalpies of solution of the extreme members in $2PbO.B_2O_3$ (970 K) have been determined, and the results have been used to study the thermochemistry of the solid solutions.[198–201]

The enthalpies of solution in $2PbO.B_2O_3$ (970 K) of the extreme members of the olivine system Mg_2SiO_4 (forsterite)–Fe_2SiO_4 (fayalite) made it possible to study a model of the molecular activity of silicate minerals#, of considerable importance for carrying out calculations for natural systems.[202–204] The determination of the enthalpies of solution in $2PbO.B_2O_3$ (1036 K) of minerals of the pyroxene group ($MgCaSi_2O_6$, $NiCaSi_2O_6$, $MnSiO_3$) and the enthalpies of fusion of $CaMgSi_2O_6$ (diopside) and $CaMgSi_2O_6$ (diopside glass),[205] and also the enthalpies of solution of cobalt silicates (α-Co_2SiO_4, β-Co_2SiO_4, γ-Co_2SiO_4), synthesised at a high pressure, made it possible to construct the $p-T$ diagrams for SiO_2-MO silicate systems.[206] The thermochemistry of the glasses and solid and liquid phases in the systems $CaMgSi_2O_6$–$CaAl_2Si_2O_8$–$NaAlSi_3O_8$, SiO_2–$CaAl_2Si_2O_8$–$NaAlSi_3O_8$, SiO_2–Al_2O_3–CaO–Na_2O, and $NaAlSi_3O_8$–$KAlSi_3O_8$ [determination of

Table 5. Enthalpies of solution of oxides (ΔH^0_T, kcal mole^{-1}) in high-temperature solvents based on B_2O_3, MoO_3, and V_2O_5.

Oxide	T, K	ΔH^0_T	Refs.	T, K	ΔH^0_T	Refs.	T, K	ΔH^0_T	Refs.
	$9PbO.3CdO.4B_2O_3$			$2PbO.B_2O_3$			$3Na_2O.4MoO_3$		
BeO	98	3.45±0.2	[237]	—	—	—	958	1.0±0.3[a]	[147]
SrO	—	—	—	967	−25.41±0.02	[221]	958	−47.9±0.9[a]	[147]
BaO	—	—	—	967	−31.00±0.02	[221]	958	−61.7±0.6[a]	[147]
ZnO	970	4.26±0.12	[222]	970	4.28±0.20	[197]	970	−3.2±0.6	[222]
ZnO	—	—	—	1173	4.86±0.05	[183]	—	—	—
CdO	970	2.71±0.03	[222]	1173	2.98±0.06	[183]	970	−9.59±0.07	[222]
CdO	958	−15.9±0.6[a]	[147]	967	2.53±0.05	[221]	—	—	—
CdO	970	5.72±0.15	[222]	970	5.95±0.15	[197]	970	−4.90±0.09	[222]
CoO	—	—	—	986	5.38±0.26	[210]	958	−6.4±0.4[a]	[147]
CoO	—	—	—	973	5.66±0.19	[228]	—	—	—
NiO	970	9.96±0.18	[222]	970	8.66±0.18	[197]	970	−0.77±0.07	[222]
NiO	—	—	—	986	8.56±0.35	[205]	958	−10.6±0.7[a]	[147]
NiO	—	—	—	1173	10.94±0.12	[183]	—	—	—
CuO	970	9.14±0.09	[222]	986	8.52±0.27	[227]	970	2.65±0.05	[222]
CuO	—	—	—	1173	12.41±0.10	[183]	958	4.3±0.7[a]	[147]
Fe_2O_3	970	16.72±0.11	[222]	973	18.04±0.45	[225]	970	−0.49±0.05	[222]
Fe_2O_3	—	—	—	974	16.68±0.12	[216]	974	−0.41±0.02	[216]
Ga_2O_3	970	8.07±0.15	[222]	974	7.50±0.09	[216]	974	5.86±0.09	[216]
In_2O_3	—	—	—	—	—	—	974	−17.83±0.14	[216]
Cr_2O_3	—	—	—	1173	5.35±0.08	[183]	—	—	—
TiO_2	—	—	—	971	3.53±0.10[i]	[219]	943	2.38±0.09[g]	[222,180]
Fe_2O_3	970	16.7±0.11	[222]	973	18.04±0.45	[225]	970	−0.49±0.05	[222]
Ga_2O_3	970	8.07±0.15	[222]	—	—	—	—	—	—
Cr_2O_3	—	—	—	1173	5.35±0.08	[183]	—	—	—
PbO	1073	3.5±0.2	[152]	967	4.15±0.06	[223]	953	−18.42±0.33[a]	[147]
GeO_2	970	−6.22±0.11	[222]	970	−4.70±0.16	[197]	—	—	—
GeO_2	966	0.5±0.2[d]	—	967	0.50±0.07	[221]	—	—	—
GeO_2	966	−8.4±0.5[b]	—	986	−4.96±0.17	[227]	—	—	—
B_2O_3	—	—	—	973	9.97±0.12	[228]	974	7.91±0.02	[216]
CuO_2	—	—	—	1173	18.80±0.18	[183]	—	—	—
Mn_2O_2	—	—	—	—	—	—	970	16.56±0.15	[222]
WO_3	1116	(3.81±3.53)[c]	[160]	973	−14.07±0.14	[224]	970	7.24±0.18	[154]
MoO_3	—	—	—	—	—	—	973	2.47±0.07	[244]

Notes. [a] solvent V_2O_5; [b] quartz structure; [c] solvent $2.5Na_2O.1.5P_2O_5$, mole fraction $N_{Na_2O} = 0.5–0.61$; [d] solvent $2PbO.B_2O_3$, tetragonal structure; [e] solvent $2PbO.B_2O_3$, hexagonal structure; [f] solvent $2PbO.B_2O_3$, vitreous; [g] rutile; [h] solvent $0.5LiBO_2 + 0.5NaBO_2$; [i] solvent $3Na_2O.4MoO_3$.

The enthalpies of formation of the solid solutions of the Mg_2SiO_4–Fe_2SiO_4 system were studied by measuring the enthalpies of solution in molten $LiBO_2$–$NaBO_2$ in a medium of argon at 1180 K.[220]

the enthalpies of solution in $2PbO.B_2O_3$ (970 K, 986 K) and the heat content $H_T - H_{298}$ (mixing in HTMC)] has been studied.[140,207,208] The results obtained were used to carry out a thermodynamic study of models of the phase equilibria for the liquid surfaces of the ternary systems and general models of the structures of geological magma.[209,210,211,212]

The extensive accumulation of material on the high-temperature microcalorimetry of silicate and oxide systems has made it possible to distinguish the corresponding mineral associates of practical importance in geochemistry, petrology, geothermometry, and silicate technology.[213,214,215,216,217] The use of thermochemical data to construct $p-T$ diagrams has been reviewed.[218] At present, high-temperature solution microcalorimetry is used to study "dry" systems. The problem of the study of hydrated chemical compounds (minerals) is at an initial stage of development. Thus an attempt has been made[219] to measure the enthalpies of aqueous solutions at a pressure of 2 kbar and 1073 K by a combined method involving high-temperature microcalorimetry and the use of high-pressure ampoules. The difficulties in studies of this kind are associated with various technical problems in the construction of the calorimetric apparatus.

3. Chemical Compounds

A second direction taken by studies in high-temperature solution microcalorimetry arose in connection with the need to determine the thermochemical characteristics of refractory substances,[197,213,221,229] which cannot be studied by other thermochemical methods. From the methodological viewpoint, the two directions, that is the thermochemistry of minerals and the thermochemistry of inorganic substances, represent a single whole, since they use similar procedures (the same measurement temperature, solvent composition, thermochemical cycle, etc.), and the materials studied as models of minerals are often products of the chemical industry. The difference between these two directions is determined only by the purposes of the studies.

Since the separate aims of the thermochemistry of inorganic substances are fairly varied, the results of the studies have been systematised in the present work on the basis of the method of study used. The main problem in the development of a procedure is the choice of solvent, in which the enthalpy of formation is determined by measuring the enthalpies of solution of the compound being studied and its components under identical conditions (solvent composition, temperature of the experiment, and concentration of dissolved substances). For example, for complex oxides (chromites, silicates, tungstates, molybdates, gallates, manganates, aluminates, ferrites, etc.), the thermochemical cycle is as follows:

$$MWO_4(\text{crystalline}) + (\text{solvent}) \rightarrow M^{2+}(\text{liquid}) + WO_4^{2-}(\text{liquid}) + (\Delta H_T^0)_1 \quad (1)$$

$$MO(\text{crystalline}) + WO_3(\text{crystalline}) + (\text{solvent}) \rightarrow M^{2+}(\text{liquid}) + WO_4^{2-}(\text{liquid}) + (\Delta H_T^0)_2 \quad (2)$$

$$MO(\text{crystalline}) + WO_3(\text{crystalline}) \rightarrow MWO_4(\text{crystalline}) + (\Delta H_T^0)_2 - (\Delta H_T^0)_1 \quad (3)$$

The known values of the enthalpies of formation of the oxides and the values obtained for $(\Delta H_T^0)_1$ and $(\Delta H_T^0)_2$ are used to calculate the enthalpy of formation of the compound. A similar procedure is used in the study of the thermochemistry of solid solutions or isomorphous mixtures, but instead of oxide mixtures [reaction (2)], a mixture of the compounds forming the required solid solution is used.[224]

Vanadium(V) oxide (V_2O_5). Kleppa[225] used molten vanadium(V) oxide as a solvent to measure the enthalpies of solution of PbO and lead vanadates with the compositions $Pb_2V_2O_7$, $Pb_3(VO_4)_2$, and $Pb_8V_2O_{13}$ at 953 K to determine the enthalpies of formation of the vanadates from the oxides. The enthalpies of solution of the oxides of the alkaline earth metals and various transition metals were measured in the samel solvent[147] at 958 ± 5 K (Tables 3 and 5).

Table 6. Enthalpies of solution of oxides (ΔH_T^0, kcal mole^{-1}) in high-temperature solvents based on B_2O_3 and MoO_3.

Oxide	ΔH_{975}^0	ΔH_{973}^0 [242, 244]	ΔH_{974}^0 [216]	ΔH_{1075}^0 [216]
	$2PbO \cdot B_2O_3$	$3Na_2O \cdot 4MoO_3$		
La_2O_3	−4.82±0.01[a]	−75.4±1.8	−81.5±0.6	−62.1±0.4
Nd_2O_3	−3.30±0.13[a]	−81.1±1.0	—	−60.3±0.3
Sm_2O_3	−3.5±0.01[a]	−75.3±1.2	−73.6±0.2	−59.9±0.4
Eu_2O_3	33.37±0.44[c]	−50.5±0.7	—	—
Gd_2O_3	−3.68±0.03[a]	−70.2±1.0	−49.3±0.4	−49.5±0.7
Dy_2O_3	−9.92±0.32[b]	−48.6±0.5	—	—
Ho_2O_3	−14.09±0.29[b]	−44.4±1.0	—	—
Er_2O_3	—	−44.9±0.5	−46.1±0.2	—
Tu_2O_3	−17.84±0.03[b]	—	−45.1±0.3	—
Yb_2O_3	—	−41.1±0.5	−42.5±0.4	−38.7±0.3
Lu_2O_3	−10.87±0.09[b]	−37.2±0.8	—	—
Y_2O_3	4.95±0.44[c]	−53.0±0.6	—	43.8±0.1
Sc_2O_3	—	−32.2±0.8	—	31.4±0.1
Pr_6O_{11}	—	−129.2±1.0	—	—
Ce_2O_3	—	—	−32.5±0.4	—

Notes: [a]mixture of $0.5Ln_2O_3 + 0.5Al_2O_3$; [b]mixture of $1.5Ln_2O_3 + 2.5Al_2O_3$;[234] [c]mixture of $0.5Ln_2O_3 + 0.5Fe_2O_3$.[231,232]

Note. Numbers in square brackets denote references (Ed. of Translation).

Table 7. Enthalpies of solution of compounds in high-temperature solvents based on B_2O_3 and MoO_3 (ΔH_T^0, kcal mole^{-1}).

Compound	ΔH_{970}^0	Refs.	Compound	T, K	ΔH_T^0	Refs.
	$3Na_2O \cdot 4MoO_3$			$2PbO \cdot B_2O_3$		
$MgMnO_4$	10.42±0.15	[222]	$MgCr_2O_4$	1173	18.48±0.1	[183]
$CoMn_2O_4$	15.44±0.12	[222]	$NiCr_2O_4$	1173	17.56±0.13	[183]
$NiMn_2O_4$	15.31±0.08	[222]	$CuCr_2O_4$	1173	15.26±0.22	[183]
$CuMn_2O_4$	16.17±0.18	[222]	$ZnCr_2O_4$	1173	25.25±0.12	[183]
$ZnMn_2O_4$	19.92±0.17	[222]	$CdCr_2O_4$	1173	18.42±0.14	[183]
$CdMn_2N_4$	14.46±0.05	[222]	Ca_2SiO_4	967	4.40±0.29	[221]
Mg_2TiO_4	−9.32±0.11	[222]	Sr_2SiO_4	967	−1.96±0.19	[221]
Co_2TiO_4	−1.38±0.11	[222]	Ba_2SiO_4	967	0.33±0.05	[221]
Zn_2TiO_4	−3.19±0.10	[222]	Cd_2SiO_4	967	12.95±0.12	[221]
$ZnNiTiO_4$	2.00±0.17	[222]	Be_2SiO_4[c]	970	7.95±0.15	[237]
$ZnCoTiO_4$	0.0±0.2	[222]	Mg_2SiO_4	965	10.2±0.2	[197]
$MgWO_4$	16.07±0.25	[154]	Pb_2SiO_4	967	11.45±0.04	[223]
$CoWO_4$	16.74±0.11	[154]	Pb_4SiO_6	967	18.57±0.25	[223]
$NiWO_4$	17.04±0.22	[154]	$PbSiO_3$	967	7.55±0.09	[223]
$CuWO_4$	16.52±0.20	[154]	Ca_2GeO_4	967	2.87±0.24	[221]
$ZnWO_4$	14.11±0.17	[154]	Sr_2GeO_4	967	−11.59±0.31	[221]
$CoWO_4$	16.58±0.05	[154]	Ba_2GeO_4	967	−5.95±0.12	[221]
Fe_2TiO_5[a]	−0.10±0.10	[240]	Cd_2GeO_4	967	14.60±0.17	[221]
α-$CdTiO_3$[a]	−0.6±0.1	[257]	$CuGeO_3$	986	8.82±0.22	[227]
β-$CdTiO_3$[a]	−4.17±0.15	[257]	$Co_3B_2O_6$	973	26.48±0.19	[228]
$Mg_3B_2O_6$[b]	16.56±0.21	[248]	$Co_2B_2O_5$	973	16.82±0.11	[228]
$Mg_2B_2O_5$[b]	23.85±0.33	[248]	CoB_4O_7	973	−9.32±0.26	[228]
MgB_4O_7[b]	31.9±1.0	[248]	$CoGeO_4$	965	21.5±0.3	[197]
—	—	—	$NaAlO_2$	975	4.70±0.11	[236]
—	—	—	$KAlO_3$	975	−0.07±0.12	[236]
—	—	—	Na_2CO_3	975	31.84±0.25	[236]
—	—	—	K_2CO_3	975	29.36±0.25	[236]

Notes: [a]T = 965 K; [b]T = 973 K; [c]solvent $9PbO.3CdO.4B_2O_3$.

A solvent melt with the composition $2PbO.B_2O_3$ was proposed by Kleppa[152] for the study of the enthalpies of solution of MgO, α-Al_2O_3, and $MgAl_2O_4$, and has since been widely used (Tables 5–9). The enthalpies of formation of magnesium silicates and aluminates at 973 K and 1173 K [180] and of magnesium, nickel, copper, zinc, and cadmium chromites with the composition MCr_2O_4 at 1173 ± 2 K,[183] determined from the measured enthalpies of solution of the compounds and the original oxides, have been used to study the thermodynamic and crystal-chemical characteristics of the formation of chromite spinels[226] and the acid–base properties of transition metal oxides.

Table 8. Enthalpies of solution of compounds in high-temperature solvents based on B_2O_3 and V_2O_5 (ΔH^0_T, kcal mole^{-1}).

Compound	ΔH^0_{970}	Refs.	Compound	T, K	ΔH^0_T	Refs.
$9PbO\cdot3CdO\cdot4B_2O_3$			V_2O_5			
$BeAl_2O_4$	15.05±0.15	[237]	$Pb_2V_2O_7$	953	9.91±0.33	[148]
$BeAl_6O_{10}$	23.35±0.23	[237]	$Pb_3V_2O_8$	953	−1.75±0.63	[148]
$ZnAl_2O_4$	22.42±0.26	[222]	$Pb_8V_2O_{13}$	953	−92.9±4.4	[148]
$CdAl_2O_4$	5.82±0.17	[222]	$CaMgB_2O_5$[a]	973	18.42±0.44	[401]
$CuAl_2O_4$	11.57±0.14	[222]	$CaWO_4$[c]	973	12.54±0.16	[400]
$CoAl_2O_4$	22.22±0.14	[222]	$MnWO_4$[c]	940	39.55÷47.92	[250]
$NiAl_2O_4$	18.30±0.15	[222]	$FeWO_4$[c]	940	31.24÷42.28	[250]
$ZnFeAlO_4$	22.8±0.2	[222]	$Fe_{0.5}Mn_{0.5}WO_4$[c]	940	40.5÷45.1	[250]
$MgGa_2O_4$	15.49±0.17	[222]	$MgGeO_4$[b]	970	11.31±0.30	[197]
$ZnGa_2O_4$	20.78±0.13	[222]	$MgGeO_3$[b]	970	5.31±0.19	[197]
$CdGa_2O_4$	12.60±0.12	[222]	$CoGeO_4$[b]	965	21.5±0.3	[197]
$CuGa_2O_4$	13.25±0.22	[222]	$CoGeO_3$[b]	965	8.65±0.21	[197]
$CoGa_2O_4$	21.32±0.15	[222]	Zn_2GeO_4	965	14.65±0.30	[197]
$NiGa_2O_4$	18.95±0.15	[222]	Co_2SiO_4	965	16.02±0.3	[197]
$MgFe_2O_4$	19.46±0.14	[222]	Zn_2SiO_4	965	15.37±0.40	[197]
$CoFe_2O_4$	28.33±0.09	[222]	Ni_2SiO_4	965	19.64±0.38	[197]
$NiFe_2O_4$	27.90±0.09	[222]	—	—	—	—
$CuFe_2O_4$	20.81±0.14	[222]	—	—	—	—
$ZnFe_2O_4$	23.63±0.16	[222]	—	—	—	—
$CdFe_2O_4$	17.66±0.17	[222]	—	—	—	—
Co_2GeO_4	19.28±0.33	[222]	—	—	—	—
Ni_2GeO_4	23.22±0.33	[222]	—	—	—	—

Notes: [a]solvent $2PbO.B_2O_3$; [b]solvent $9PbO.3CdO.4B_2O_3$; [c]solvent $0.51LiBO_2 + 0.5NaBO_2$, mole fraction of tungstate 0.00345–0.0258 and 0.0012–0.0252 respectively.

The energy characteristics and stability of the structures of silicates and germanates of the transition metals (Co, Ni, Zn) and magnesium,[197] the alkaline earth metals (Ca, Sr, Ba) and cadmium,[221] and minerals based on them have been studied by measuring the enthalpies of solution of the silicates, germanates, and corresponding oxides at (965–967) ± 2 K. A lead borate solvent has been used successfully by a number of authors to study the thermochemistry of the phases formed in the systems $PbO–SiO_2$ ($PbSiO_3$, Pb_2SiO_4, Pb_4SiO_6),[223] $CuO–GeO_2$ ($CuGeO_3$),[227] and $CoO–B_2O_3$ ($Co_3B_2O_6$, $Co_2B_2O_5$, CoB_4O_7)[228] in the thermochemistry of solid solutions.[140,224,229]

The thermochemistry of ferrites, borates, aluminates, and gallates with the composition§ $LnMoO_3$ (Ln represents a lanthanide, yttrium, or scandium) at 974, 975, and 1075 K [216,230–233] and aluminates[234,235] with the compositions $LnAlO_3$ and $Ln_3Al_5O_{12}$ at 875 K has been studied by measuring the enthalpies of solution of the compounds and the corresponding oxides of the lanthanides, iron, boron, aluminium, and gallium. The enthalpies of solution of sodium and potassium aluminates and carbonates at 975 K have been used to determine the enthalpies of formation of $NaAlO_2$ and $KAlO_2$.[236]

§ In the compounds $LnMO_3$. M represents Fe, B, Al, or Ga.

Table 9. Enthalpies of solution of compounds of the lanthanides in melts based on B_2O_3 or MoO_3 [216,230,234,244,245,246,243] (ΔH^0_T, kcal mole^{-1}).

Ln	$LnAlO_3$[b], (975 K)	$Ln_2(MoO_4)_3$[a], (973 K)	$NaLn(MoO_4)_2$[a], (973 K)	$LnBO_3$[a] (974 K)	$LnGaO_3$ or (Ln_2FeO_4)(974 K)
La	9.50±0.20	−0.26±0.14	21.6±0.4	7.34±0.05	−20.6±0.2[a]
La	−15.40±0.07[c]	—	—	—	(−19.10±0.17[c])
Pr	—	8.81±0.34	18.3±0.7	—	—
Nd	8.03±0.72	9.71±0.47	17.4±0.5	9.34±0.12[b]	1.05±0.07[b]
Nd	−14.22±0.12[c]	—	—	—	(4.78±0.07[b])
Sm	7.29±0.15	12.81±0.18	17.3±0.7	5.2±0.2[c,e]	(−16.47±0.05)[c]
Sm	−10.68±0.05[c]	—	—	9.01±0.07[b,e]	—
Eu	—	3.20±0.10	19.3±0.5	10.40±0.05[b]	(29.77±0.11[b])
Gd	5.31±0.12	16.20±0.88	16.9±0.4	7.4±0.2	—
Gd[e]	—	20.70±1.36	—	—	—
Tb	—	—	—	7.07±0.02[b]	—
Dy	32.22±0.35[d]	3.05±0.15	17.0±0.8	10.35±0.07[b]	—
Ho	34.58±0.22[d]	2.86±0.25	20.0±0.5	10.49±0.12[b]	—
Er	—	21.4±1.1	20.2±0.6	4.04±0.05	—
Yb	—	15.71±0.82	18.8±0.5	6.43±0.07[c]	—
Lu	32.71±0.14[d]	14.7±0.5	20.4±0.4	4.64±0.07[b]	—
Y	7.62±0.09	19.79±0.64	19.0±0.5	11.21±0.07[b]	(−16.30±0.14[c])
Tu	41.07±0.43	—	—	4.67±0.20	—
Sc	−15.4±0.07[c]	7.23±0.17	2.2±0.3	4.06±0.10[b]	(−14.84±0.12)[c]
Ce	1.23±0.02[a]	—	—	15.4±0.2	2.99±0.02[a]

Notes: [a]solvent $3Na_2O.4MoO_3$; [b]solvent $2PbO.B_2O_3$; T = 974 K or 975 K; [c]solvent $3Na_2O.4MoO_3$; T = 1075 K; [d]aluminate with the composition $Ln_3Al_5O_{12}$; [e]forms of $LnBO_3$ or $Gd_2(MoO_4)_3$.

Molten $9PbO.3CdO.4B_2O_3$. Beryllium aluminates and silicate (and also BeO, Al_2O_3, SiO_2) dissolve more readily in a melt with the composition $9PbO.3CdO.4B_2O_3$.[237] This solvent was therefore used[197] to refine the results of the study of the solution of MgO and various metal silicates and germanates, and also for a thermochemical study of the aluminates, ferrites, gallates, and germanates of bi- and tervalent metals.[222]

Molten $3Na_2O.4MoO_3$. A number of solvent melts based on MoO_3 are known.[139,155,156,238,239] The most widely encountered is the melt with the composition $3Na_2O.4MoO_3$, first used by Navrotsky and Kleppa.[155] The enthalpies of solution of simple and complex oxides of the transition metals in this melt were measured in a cycle of studies to determine the enthalpies of formation of the titanates M_2TiO_4 [222,240] and manganates M_2MnO_4 [222] with the spinel structure, and the isostructural tungstates MWO_4;[154,241] the thermodynamic data were compared with the mechanism of spinel formation by the titanates and manganates, and the thermodynamic characteristics of the tungstates were compared with the data for the sulphates, carbonates, and silicates of the same metals.

A systematic study of the thermochemistry of lanthanide molybdates has been carried out.[242–247] The enthalpies of formation of simple and double lanthanide molybdates were determined for the first time by measuring the enthalpies of solution of the oxides Ln_2O_3, Pr_6O_{11}, and MoO_3 and the molybdates $Ln_2(MoO_4)_3$, and $NaLn(MoO_4)_2$, and Na_2MoO_4 at 973 ± 0.5 K and of $Na_4La(MoO_4)_4$ at 897 K. The enthalpies of formation of magnesium borates were determined[248] from data on the composition of the compounds formed in the $MgO–B_2O_3$ system and the enthalpies of solution of the

borates $Mg_3B_2O_6$, $Mg_2B_2O_5$, and MgB_4O_7 and the oxides MgO and B_2O_3, measured at 973 ± 2 K.

Molten $NaPO_3$–$Na_4P_2O_7$. A relatively new solvent melt with the composition $2.5Na_2O.1.5P_2O_5$, proposed by Ko and Kleppa,[160] has been used to measure the enthalpies of solution of WO_3 in the presence of Na_2O (1116 K). There are no published data on other studies with this solvent.

Molten $LiBO_2$–$NaBO_2$. The enthalpies of formation of the solid solutions formed by manganese and iron tungstates have been determined[249,250] by measuring the enthalpies of solution of the solid solutions and oxides of tungsten(VI), iron(II), and manganese(II) in a solvent with the composition $0.5LiBO_2 + 0.5NaBO_2$ at 940 K¶.

Molten KCl–LiCl. A eutectic melt of lithium and potassium chlorides has been used[251] to measure the enthalpies of solution of the double chlorides of caesium and the transition metals (and calcium) at 728 K, to determine the enthalpies of formation (Table 9) and to study the stability of the ions in the melts. The enthalpy of the reaction of lead oxide (PbO) with liquid cadmium in the working cell at 800 K, measured by mixing, was −39.58 ± 0.89 cal mole^{-1} PbO.[252] Concentrated sulphuric acid has been used as solvent.[253] The authors cited measured the enthalpies of solution of copper and cadmium selenochromites and Cu(Cd) + Cr + Se mixtures at 475 K, and calculated the enthalpies of formation of the selenochromites, which have the spinel structure. The results, together with the data for other transition metal sulphides and selenides,[253] were used to study the energies of formation in oxide–sulphide–selenide series and to examine the characteristic features of the formation of chalcogenide spinels. The results of the measurements of the enthalpies of solution of the oxides are given in Tables 5 and 6, and the enthalpies of the chemical compounds in Tables 7–10.

Table 10. Enthalpies of solution of chlorides in a high-temperature solvent (ΔH^0_T, kcal mole^{-1}).

M	MCl_2	$CsMCl_3$	Cs_2MCl_4	Cs_3MCl_5
Mn	2.75±0.04	14.08±0.04	12.24±0.08	14.31±0.10
Fe	3.63±0.04	14.88±0.06	14.11±0.11	15.90±0.13
Co	2.44±0.20	13.47±0.13	16.51±0.14	17.77±0.15
Ni	9.48±0.01	20.32±0.18	—	15.01±0.22
Cu	1.23±0.30	11.25±0.30	11.55±0.25	14.05±0.32
Zn	−3.75±0.30	—	15.90±0.21	16.60±0.10
Zn	−6.20±0.30[b]	—	—	—
Ca	1.04±0.13	12.52±0.03	—	—
Cs[a]	1.46±0.02	—	—	—

Notes: [a] CsCl; [b] $ZnCl_2$(liquid).

Data on calcium, magnesium, and lead silicates have been used in a comparison of the results of the determination of the enthalpies of formation of silicates from the oxides by classical calorimetry involving solution in aqueous acid solutions (hydrofluoric acid) and high-temperature microcalorimetry involving solution in solvent melts (Table 11).

¶ The enthalpies of solution of $Fe_{1-x}O$ (where x = 0.0485 to 0.1166) in the same melt at 1179 K have been measured.[405]

Table 11. Comparison of the enthalpies of formation of silicates from the oxides (kcal mole^{-1}), determined by high-temperature solution microcalorimetry in molten $2PbO.B_2O_3$ (I) and solution calorimetry in aqueous HF (II) at 298 K.

Compound	Method I	Method II
$CaSiO_3$	−21.01±0.25 [137]	−21.25±0.11 [125]
$MgSiO_3$	−7.61±0.27 [17]	−8.69±0.15 [125]
Mg_2SiO_4	−13.90±0.33 [17]	−15.12±0.21 [125]
Mg_2SiO_4	—	−13.86±0.30 [135]
$CaMgSi_2O_6$	−34.99±0.41 [137]	
$CaMgSi_2O_6$	−33.35±0.47 [184, 185]	−35.25±0.22 [135]
$PbSiO_3$	−4.3±0.3 [223]	−4.2±0.5 [134]

Note. Numbers in square brackets denote references (Ed. of Translation).

4. Phase Transformations

High-temperature solution microcalorimetry can be used to study the enthalpies of phase transformations by successively dissolving the two phases of the same chemical compound (mineral) under identical conditions (temperature, solvent composition, solute concentration). The enthalpy of a phase transformation is generally small (often <0.5 kcal mole^{-1}), and since it is determined from the difference between the large values of the enthalpies of solution of the two phases, the uncertainty is high,[86,196,254] and amounts to ~0.2 kcal mole^{-1}. Much better results can be obtained by the direct determination of the enthalpy of the transformation by simultaneously dissolving the two phases in the two cells of a differential HTMC.[229,255] These methods have been used to study the enthalpies of polymorphic transformations, phase transformations, and fusion, the enthalpies of formation of solid solutions, and the enthalpies of processes involving the disordering of solid phases, by dissolving the appropriate specimens in melts with the compositions $3Na_2O.4MoO_3$,[256,257,229] $2PbO.B_2O_3$,[181,196,205,254,258–265] $9PbO.3CdO.4B_2O_3$,[86,104,164,266] and $LiBO_2$–$NaBO_2$ [220] (Table 12).

Table 12. Enthalpies of phase transformations, determined by dissolving the phases in a melt (ΔH^0_T, kcal mole^{-1}).

Compound	Transformation	T, K	ΔH^0_T	Refs.
Al_2O_3	α→γ	978	−5.3	164
Al_2O_3	κ→α	978	3.6	164
Al_2O_3	δ→α	978	−2	164
SiO_2	quartz → coesite	970	0.7±0.1	86
SiO_2	quartz → stishovite	970	1.4±0.1	86
SiO_2	quartz → cristobalite	970	0.45±0.15	86
SiO_2	cristobalite → liquid	966	2.5±0.2	86
Ni_2SiO_4	olivine → spinel	986	1.4±0.7	254
$CaSiO_3$	β → α	971	1.26±0.31	196
$MnSiO_3$	rhodonite → pyroxyoptite		0.1±0.3	205
$CaMgSi_2O_6$	diopside → glass	986	21.0±0.3	205
Al_2SiO_5	andalusite → sillimanite	973	0.67±0.23	168
$Mg_2Al_4Si_5O_{18}$	cordierite-K → cordierite glass	963	54±2	181
TiO_2	brookite → rutile	971	−0.17±0.09	256
TiO_2	anatase → rutile	971	−0.78±0.20	256
TiO_2	anatase → rutile	968	−1.57±0.15	225
$CdTiO_3$	α → β	965	3.58±0.18	257
GeO_2^*	tetragonal → hexagonal	965	5.18±0.25	408
GeO_2^*	hexagonal → vitreous	965	3.7±0.6	408

*Phase transformations: tetragonal structure → hexagonal structure, hexagonal structure → vitreous phase.

IV. THERMOCHEMICAL STUDY OF GAS–SOLID REACTIONS

High-temperature microcalorimetry can be used to measure the enthalpies of heterogeneous solid + gas chemical reactions. Procedures for measuring the enthalpies of oxidation were examined in detail in a study of the oxidation of niobium.[267] The influence of the oxygen pressure and the temperature of the experiment on the form of the heat-liberation curve was studied, and the thermal effects of the successive stages of the oxidation: the dissociation and adsorption of oxygen, diffusion, and the formation of compounds on the surface, were examined. The results of this study were used to develop a method for the microcalorimetric study of heterogeneous reactions of solids with gases to give new solid compounds.

The calorimeter for the study of M + O_2 systems is calibrated from the known enthalpy of oxidation to give an oxide with a definite composition, or from the enthalpy of another chemical reaction.[268] Since the calibration constant may change from one experiment to another (for example, $K_1 = 100$, $K_2 = 120$, $K_3 = 130$), but remains constant during a given experiment, the HTMC are calibrated immediately before the experiment or immediately after it.[93] The enthalpy of the oxidation of thorium to ThO_2 has been recommended[93] for calibration. In the study of M + H_2 systems, the calibration is carried out either electrically or by mixing, since the partial enthalpies of solution of hydrogen are ~10 kcal, and in this case the quantity $0.5RT \cong 0.7$ kcal mole^{-1} cannot be neglected; it can be neglected, however, for the enthalpies of solution of oxygen (oxidation), amounting to ~80 kcal[268] ($0.5RT \cong 1.3$ kcal mole^{-1}).

The procedure involving the study of gas + solid reactions was used to measure the enthalpies of the oxidation of metals by oxygen.[95] Kleppa and co-workers[269–272] measured the enthalpies of the oxidation of tungsten, vanadium, niobium, and tantalum and the lower oxides of tungsten, vanadium, and titanium to give WO_3, V_2O_5, NbO_x, and TiO_2 respectively at temperatures of ~1100 K, and the heat of solution of O_2 in the non-stoichiometric phase TiO_x at 1323 K has been measured.[273] A similar procedure was used[274,275] to measure the enthalpies of oxidation of the lower oxides of praseodymium and terbium at 713 K and of the lower oxides of cerium ($CeO_{1.5}$–$CeO_{1.95}$) at 1353 K,[94] plutonium ($PuO_{1.5}$–$PuO_{1.71}$), and uranium[277,276,97] to give CeO_2, $PuO_{1.61}$, PuO_2, and U_3O_8 respectively. The enthalpies of oxidation of cerium oxides[94] have been compared with the results obtained by studying the equilibrium $CeO_{1.5} + O_2 \rightleftharpoons CeO_2$; the difference in the enthalpies of oxidation for the composition $CeO_{1.86}$ is less than 3 kcal. The uncertainty of the measurements of the enthalpies of oxidation of plutonium oxides[278] was 2%. The enthalpies of oxidation of non-stoichiometric iron oxides (FeO_{1+x}) were studied at 1073 K for $x = 1.05$–1.109 and at 1348 K for $x = 1.040$–1.140.[96,98,279] The partial enthalpies of solution of oxygen were measured; for the compositions FeO_{1+x} ($x = 0.040$–0.140), the enthalpies of mixing were 120.2–133.6 kcal mole^{-1}, and the values given for ΔH^0_{0x} increase linearly with increase in Δx.

The enthalpy of the chemisorption of oxygen on zinc powder has been determined[280] at 303.7 K and 451.1 K. The values obtained from the results of 15 experiments at 303.7 K (165–170 kcal mole^{-1} O_2) and at 451.1 K (166.0–176 kcal mole^{-1} O_2) are close to the standard enthalpy of formation of ZnO ($\Delta H^0_{f\,298} = -167.6$ kcal mole^{-1} O_2). The results confirm that it is possible in principle to use high-temperature microcalorimetry to study gas–solid reactions, and also that the method is suitable for the study of sorption processes and the reactions involved in the formation of non-stoichiometric compounds.

The adequate reliability of the measurements of the enthalpies of oxidation of "comparatively simple materials" (metals and oxides) enabled a number of authors to use the same procedure to study the oxidation of more complex oxygen compounds. Thus the enthalpy of oxidation of titanium oxide nitride at 1500 K according to the scheme:

$$TiO_xN_y + 0.5\,x\,O_2 \rightarrow TiO_2 + 0.5\,y\,N_2$$

has been determined.[281] Since the procedure is fairly complicated, the uncertainty of the experiment was estimated as 5%, which is greater than that of other microcalorimetric procedures, for example that involving the measurement of enthalpies of solution. The enthalpy of oxidation of cerium orthoferrite by atmospheric oxygen according to the equation:

$$CeFeO_3 + 0.25\,O_2 \rightarrow CeO_2 + 0.5\,Fe_2O_3$$

was measured at 975 K [282] by dropping the specimens, brought to constant temperature at 298 K, into the calorimeter cell. A similar procedure was used[258,283] to determine the enthalpies of oxidation of double sulphides of cobalt, iron, molybdenum, gallium, and copper. The enthalpies of the reactions of the type:

$$CoCr_2S_4 + 7\,O_2 \rightarrow CoCr_2O_4 + 2\,SO_2 + 2\,SO_3 \quad (975\ K)$$
$$Ga_{2/3}Mo_2S_4 + 9.5\,O_2 \rightarrow 1/3\,Ga_2O_3 + 2\,MoO_3 + 4\,SO_3 \quad (920\ K)$$

are given in Table 13. Non-stoichiometric iron sulphides have been studied by oxidising Fe.[284] The following reaction took place in the calorimeter cell at 555 K:

$$(1-0.4\,x)\,FeS + 0.4\,x\,O_2 \rightarrow Fe_{1-x}S + 0.2\,x\,Fe_3O_4$$

with enthalpy $\Delta H^0_{555} = -(23.1 \pm 1.4)x$, and the enthalpy of formation of the sulphides is:

$$\Delta H^0_{f\,555}\,(Fe_{1-x}S) = \Delta H^0_{f\,555}\,(FeS) + (10.0 \pm 1.8)\,x,\ x = 0 - 0.125$$

The results of the study of solid + oxygen reactions indicate the extensive possibilities provided by the procedure being considered for the thermochemical study of heterogeneous solid + gas chemical reactions. This is confirmed by studies of the high-temperature thermochemistry of M + H_2 systems, which from the calorimetric viewpoint are analogous to the reactions involved in the oxidation of metals. The solution of hydrogen and deuterium in metals, alloys, or solid solutions of M–H_2 or M–D_2 systems has been studied. The partial enthalpies have been measured[285,286] for the solution of hydrogen in lanthanum, yttrium, and their hydride phases at 917 K and 919 K, in vanadium, niobium, and tantalum and their solid solutions with hydrogen at 264, 300, and 437 K (V), 356 K and 440 K (Nb), and 700 K and 703 K (Ta), and in thorium at 700 K.[287–289] The thermodynamic properties of solutions of H_2 and D_2 in palladium at 770–970 K, in manganese at 550–700 K, and in the alloys Pd–Au (10.25% and 40% Au) and Pd–Cu (10.25% and 40% Cu) at 555 K and 700 K, and Pd–Ag and Pd_3Mn at 555–909 K have been measured.[290–297]

The temperature dependence of the enthalpy of solution of hydrogen has been measured in dilute PdH_x solutions at 555–712 K [238] and in Pd at 518–625 K and pressures up to 34 atm. The reaction of H_2 and D_2 with α-Zr has been studied,[299,300] and the enthalpies of solution determined. The solution of hydrogen in $LaNi_5$–$CaNi_5$ alloys at 298 K has been studied.[287]

Most studies showed that the enthalpies of solution are practically independent of the temperature at which the measurements are made. In a series of remarkable studies,[287,290–293] the microcalorimetric procedure was combined with a flow method for studying heterogeneous equilibria (gas–solid) to determine both ΔH^0 and ΔG^0 for the formation of hydride

phases. In these studies, as in other work,[288,289] good agreement was observed between the results of the measurements by two independent methods. The combination of the results of the microcalorimetric experiment (the enthalpy of the solid + gas reaction) with the results of the study of the equilibria in the same system (the Gibbs function) makes it possible to determine more accurately the fundamental thermodynamic functions of the solid–gas system and to use them to model the geological processes involved in the reaction of minerals with hot gas mixtures (H_2, O_2, N_2), in the study of sulphide equilibria and the solid phases in meteorites,[139,140] and to construct gas–metal equilibrium diagrams in metallurgy.[93–98] Table 14 compares the enthalpies of oxidation determined by high-temperature microcalorimetry with data obtained by combustion calorimetry in an oxygen bomb.

Table 13. Enthalpies of oxidation ($-\Delta H^0_T$, kcal mole^{-1}).

Starting material	Oxidation products	T, K	$-\Delta H^0_T$	Refs.
Zn	ZnO	303.7	(165÷170)	[280]
Zn	ZnO	451.1		
W	WO_3	910	198.94	[269]
WO_2	WO_3	910	60.52±0.65	[269]
$WO_{2.72}$	WO_3	910	14.84±0.16	[269]
$WO_{2.96}$	WO_3	910	6.30±0.06	[269]
$CeO^a_{1.5}$	$CeO_{1.65}$	1353	178	[94]
$CeO^a_{1.72}$	$CeO_{1.85}$	1353	198	[94]
$CeO^a_{1.85}$	$CeO_{2.00}$	1353	222	[94]
Pr_7O_{12}	PrO_{2-x}	713	58	[274]
$TbO_{1.5+x}$	Tb_7O_{12}	713	54	[275]
$TiO_{0.81}$	TiO_2	1100	119.72±1.05	[271]
$TiO_{0.89}$	TiO_2	1100	108.24±1.35	[271]
TiO	TiO_2	1100	95.82±1.09	[271]
$TiO_{1.05}$	TiO_2	1100	89.97±1.03	[271]
$TiO_{1.17}$	TiO_2	1100	82.43±1.06	[271]
$TiO_{1.20}$	TiO_2	1100	75.75±0.63	[271]
$TiO_{1.26}$	TiO_2	1100	71.34±1.03	[271]
$TiO_{1.5}$	TiO_2	1100	45.42±0.60	[271]
$TiO_{1.67}$	TiO_2	1100	31.19±0.43	[271]
$FeO_{1.05-1.15}$	$FeO_{1.5-x}$	1348	120–134	[98]
$VO_{1.5}$	V_2O_5	910	39.35±0.42	[270]
$VO_{5/3}$	V_2O_5	910	27.26±0.31	[270]
$VO_{7/4}$	V_2O_5	910	24.16±0.40	[270]
$VO_{9/5}$	V_2O_5	910	22.75±0.30	[270]
$VO_{11/6}$	V_2O_5	910	21.71±0.23	[270]
$VO_{15/8}$	V_2O_5	910	21.0±0.30	[270]
VO_2	V_2O_5	910	14.97±0.34	[270]
$VO_{13/6}$	V_2O_5	910	8.94±0.1	[270]
$FeS + SO_2$	$Fe_{1-x}S + Fe_3O_4$	555	(23.1±1.4)x	[284]
TiO_xN_y[b]	$TiO_2 + N_2$	1500	(116.4–68.0)	[281]
$CeFeO_3$	$CeO_2 + Fe_2O_3$	975	26.10±0.30 (298 K)	[282]
UO_2	$UO_{2.242}$	1323	8.75	[410]
$Ga_{2/3}Mo_2S_4$	$Ga_2O_3 + MoO_3^+SO_3$	920	703.8±1	[283]
$PuO^a_{1.5}$	PuO_2	1373	210±5	[278]
$PuO^a_{1.61}$	PuO_2	1373	214±5	[278]
$PuO^a_{1.5}$	$PuO_{1.61}$	1373	197	[278]
$PuO^a_{1.61}$	$PuO_{1.70}$	1373	195	[278]
$PuO^a_{1.70}$	$PuO_{1.71}$	1373	175	[278]
$PuO^a_{1.71}$	PuO_2	1373	221	[278]
$CoCr_2S_4$	$CoCr_2O_4 + SO_2 + SO_3$	975	548.5±1.2	[241]
$FeCr_2S_4$	$Fe_2O_3 + Cr_2O_3 + SO_2 + SO_3$	975	565.4±1.7	[241]
$CuCr_2S_4$	$CuO + Cr_2O_3 + SO_2 + SO_3$	975	516.4±1.6	[241]

Notes: [a] kcal mole^{-1} O_2; [b] x = 0.72–0.16; y = 0.3–0.47.

Table 14. Comparison of the enthalpies of formation of oxides ($-\Delta H^0_{f\,298}$, kcal mole^{-1}), determined by high-temperature microcalorimetry from the enthalpy of oxidation and by combustion calorimetry in an oxygen bomb.

Starting material	Oxidation product	HTMC		Calorimetry	
W	WO_3	198.94	[269]	201.4±0.2	[134]
WO_2	WO_3	140.19±0.70	[269]	140.9±0.2	[134]
$WO_{2.72}$	WO_3	186.34±0.27	[269]	185.4±2.0	[134]
$WO_{2.90}$	WO_3	195.08±0.22	[269]	195.6±2.0	[134]
Zn	ZnO	82.5–85.0	[280]	83.80±0.06	[134]
$PuO^a_{1.51}$	$PuO_{2.00}$	207±7	[278]	206±2	[278]
$PuO^a_{1.57}$	$PuO_{2.00}$	210±7	[278]	208±2	[278]

Notes: [a] enthalpies of oxidation in kcal mole^{-1}; [b] T = 450 K.

Note. Numbers in square brackets denote references (Ed. of Translation).

V. THE STUDY OF THE DISSOCIATION OF SOLIDS

Studies of the enthalpies of dissociation of solids are methodologically similar to microcalorimetric studies of solid + gas reactions. The dissociation, however, is accompanied by the liberation of the gaseous reaction product from the cell, with mass exchange between the contents of the cell and the surrounding medium and the removal of heat from the measurement zone. Thus in the study of dissociation it is important to take account of corrections for the removal of heat with the liberated gas. The use of an ampoule dropped into the calorimeter cell makes it possible to avoid mass transfer of gas and corresponding heat loss.

The largest number of studies using this procedure have been devoted to crystalline hydrates and metal carbonyls. The enthalpies of dehydration of the calcium aluminates $CaAl_2O_4.10H_2O$, $Ca_2Al_2O_5.8H_2O$, and $Ca_3Al_2O_6.6H_2O$,[303] and the dissociation of potassium hydrogen phosphates,[118] accompanied by the liberation of water:

$$K_2HPO_4 \rightarrow 0.5\,K_4P_2O_7 + 0.5\,H_2O\,(\text{gas})$$
$$2\,K_2HPO_4 + KH_2PO_4 \rightarrow K_5P_3O_{10} + 2\,H_2O\,(\text{gas})$$

have been studied. The enthalpies of the reactions are given in Table 15. The enthalpy of dissociation of lithium sulphate monohydrate at 328–348 K and p = 0.7–5 mmHg is 14.7 ± 0.7 kcal mole^{-1};[304] the dissociation of calcium iodate hexahydrate at 323 K and 423 K has been studied.[305]

The dissociation of transition metal carbonyls in a double HTMC at 514, 534, and 543 K in an argon atmosphere has been studied.[306–309] The measurements were made by dropping glass ampoules with and without the substance into the differential cell. The measurements made it possible to determine the enthalpies of dissociation of Mn, Mo, and Cr carbonyls, and also the enthalpies of the reactions of the carbonyls with iodine vapour (Table 13). The enthalpies of the reactions studied were used to calculate the M–CC bond energies, where M is a transition metal. Similar methods were used[310] to study the reduction and bromination of uranium(III) oxide to the tetrabromide. The enthalpy of dissociation of lithium orthotitanate

$$Li_4TiO_4 + CO_2 = Li_2CO_3 + Li_2TiO_3$$

has been used[311] to determine the enthalpy of formation of the orthotitanate. The value obtained at 860 K and p_{CO_2} = 1 atm was 104.1 ± 0.7 kJ mole^{-1}. The dissociation of the double caesium nickel chloride, which takes place in the

solid phase, has been studied at 718 K by mixing (by dropping an ampoule containing the original Cs_3NiCl_5 [312] and repeated measurements by mixing to determine the difference $H_T - H_{298}$). A noteworthy feature of the last two methods for measuring the enthalpies of solid-phase decomposition is that the absence of gas liberation eliminates the additional experimental errors.

Table 15. Enthalpies of dissociation and iodination, kcal mole^{-1}.

Starting materials	Reaction products	T, K	ΔH_T^0	Refs.
$CaAl_2O_4 \cdot 10H_2O$	$CaAl_2O_4 + 10H_2O$	368	−35.4	[303]
$Ca_3Al_2O_5 \cdot 8H_2O$	$Ca_3Al_2O_5 + 8H_2O$	373	−16.5	[303]
$Ca_3Al_2O_5 \cdot 6H_2O$	$Ca_3Al_2O_6 + 6H_2O$	587	−88	[303]
$Ca(IO_3)_2 \cdot 6H_2O$	$Ca(IO_3)_2H_2O + 5H_2O$	323	65.87	[305]
$Ca(IO_3)_2 \cdot H_2O$	$Ca(IO_3)_2 + H_2O$	423	11.78	[305]
K_2HPO_4	$K_4P_2O_7 + H_2O$	598—653	11.0	[118]
$KH_2PO_4 + 2K_2HPO_4$	$K_5P_3O_{10} + 2H_2O$	573—673	32.4	[118]
$Cr(CO)_6$	$Cr + 6CO$	514	74±3	[306]
$Mo(CO)_6$	$Mo + 6CO$	534	81±3	[306]
$Mn_2(CO)_{10} + 2I_2$	$2MnI_2 + 10CO$	514	4.78	[306]
$Mo(CO)_6$	$Mo + 6CO$	534	81.1	[307]
$Cr(CO)_6$	$Cr + 6CO$	514	73.64	[307]
$Cr(CO)_6 + I_2$	$CrI_2 + CrI_3 + 6CO$	514	33.4	[307]
$Mn(CO)_5Br$	$0.5Mn + 0.5MnBr_2 + 5CO$	514	48.4	[308]
$Mn(CO)_5Br + 0.5\,I_2$	$MnBrI + 5CO$	514	16.6[a]	[308]
$Mn(CO)_5Cl$	$0.5Mn + 0.5MnCl_2 + 5CO$	543	37.1[a]	[308]
$Mn(CO)_5Cl + 0.5\,I_2$	$MnClI + 5CO$	514	14.5[a]	[308]
$Li_4TiO_4 + CO_2$	$Li_2CO_3 + Li_2TiO_3$	860	104.1±0.7	[311]
Cs_3NiCl_5	$CsNiCl_3 + 2CsCl$	718	7.3±0.1[a]	[312]
$Fe_2(CO)_9$	$2Fe + 9CO$	553—573	120	[309]
$Fe_2(CO)_9 + I_2$	$Fe + FeI_2 + 9CO$	524—573	118	[309]
$Fe_3(CO)_{12}$	$3Fe + 12CO$	494—544	123[a]	[309]
$Fe_3(CO)_2 + I_2$	$2Fe + FeI_2 + 12CO$	494—544	126[a]	[309]
$Co_2(CO)_8$	$2Co + 8CO$	470—475	98	[309]
$Co_4(CO)_{12}$	$4Co + 12CO$	514	124[a]	[309]
$Co_4(CO)_{12} + I_2$	$3Co + CoI_2 + 12CO$	456—518	124±4[a]	[309]
$Ru_3(CO)_{12}$	$3Ru + 12CO$	553—573	142[a]	[309]
$Rh_4(CO)_{12}$	$4Rh + 12CO$	518—574	119±3[a]	[309]
$Rh_6(CO)_{16}$	$6Rh + 16CO$	458—574	62±3[a]	[309]
$Re_2(CO)_{10}$	$2Re + 10CO$	593	129[a]	[309]
$Re(CO)_{10} + I_2$	$Re + ReI_2 + 10CO$	558—593	132[a]	[309]
$Os_3(CO)_{12}$	$30S + 12CO$	593	101[a]	[309]
$Ir_4(CO)_{12}$	$4Ir + 12CO$	594	118±4[a]	[309]
$UO_3 + 3C + 2Br_2$	$UBr_4 + 3CO$	775—878	9.1±0.2	[310]

Note: [a] T = 298 K.

VI. ENTHALPIES OF SYNTHESIS

A procedure analogous to that involving mixing in an HTMC can be used to study the enthalpies of formation of compounds during their preparation, for example during solid-phase synthesis. This method has not been widely used up to the present, however. In a study of the syntheses, the reaction of skinnerite with sulphur at 720 K to give the non-stoichiometric sulphides[313]

$$CuSbS_3 + x\,S \rightarrow CuSbS_{3+x}$$

and of liquid sulphur with FeS_x at 433 K [314] were studied. The results of the measurements [314] were used to determine the concentration dependence of the enthalpy of formation of iron sulphides, $\Delta H_{433}^0 = -22.2 \pm 11.8x$ kcal mole^{-1} for $0 \leq x \leq 0.095$ and also for $0 \leq x \leq 0.125$.

The enthalpies of formation of the double sulphides and selenides of gallium and thallium have been studied.[315] Stoichiometric mixtures of the sulphides (selenides), placed in an ampoule in the cell of an HTMC, were heated to 550—553 K for the sulphides and to 625 K for the selenides, and the enthalpy of the solid-phase synthesis on heating was determined:

$$Ga_2S_3 + Tl_2S_3 \rightarrow 2\,TlGaS_2,\ Ga_2Se_3 + Tl_2Se_3 \rightarrow 2\,TlGaSe_2$$

A similar procedure has been used to study the thermochemistry of the solid-phase reactions involved in the formation of manganese and boron carbides at 1320 K.[316,317]

VII. THERMOCHEMISTRY OF THE MIXING OF MOLTEN SALTS

The experimental study of the thermochemistry of molten salts was begun by Kleppa[38] with measurements of the enthalpies of mixing of melts of sodium and potassium nitrates at 619 K and 721 K. An ampoule containing a molten nitrate was placed in the cell of an HTMC containing the melt of the other nitrate (see Fig. 2*d*); the reaction began when the ampoule was broken using the manipulator. To increase the accuracy of the measurement, the effect of mixing was compensated by dropping specimens of gold, whose high-temperature enthalpy is known. This method was used to study the concentration dependence of the enthalpies of mixing in binary melts formed by the alkali metal nitrates[318] and in the mixtures $AgNO_3$–M^1NO_3,[319] M^1NO_3–$M^2(NO_3)_2$,[320—322] and $TlNO_3$–M^1NO_3,[323] where M^1 represents an alkali metal, and M^2 an alkaline earth metal. The enthalpies of mixing were also measured in the ternary systems formed by alkali metal nitrates with silver nitrate at $T < 723$ K.[324]

In all the systems studied, the values of the enthalpies of mixing increase regularly with increase in the differences in the sizes of the cations, but the sign of the effect shows no regularity. For most nitrate systems containing alkali metals, the enthalpies of mixing are negative. Some experimental data giving the dependence of the enthalpy of mixing on the mole fraction of a nitrate[38,318—324] are shown graphically in Fig. 7.

In spite of a theoretical treatment of the enthalpies of mixing, based on various assumptions,[325] and a review of experimental data,[318,319] regular features having "predictive power" could not be found. In accordance with the conformational theory of solutions, therefore, further studies of enthalpies of mixing were undertaken to examine the influence of the size and charge of the ions on the enthalpy of mixing.

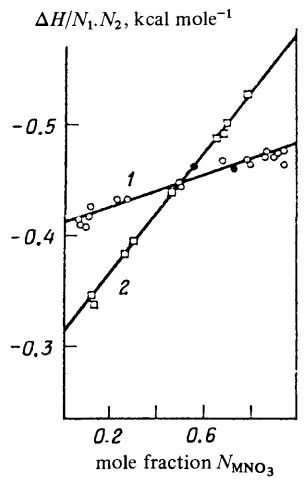


Figure 7. Dependence of the reduced enthalpy of reaction ($\Delta H/N_1.N_2$, kcal mole^{-1}) on the mole fraction of the nitrate (N_{MNO_3}) with the larger cation: *1*) KNO_3–$NaNO_3$, *2*) KNO_3–$AgNO_3$.

The enthalpies of mixing were studied for the halide systems MCl–M'Cl,[89–91,326,327] MCl–M'Cl–AgCl,[116,328] MCl–MCl_2,[329–333] MBr–MBr_2,[334] MCl_2–$M'Cl_2$,[335–338] and MI–M'I,[339] and the halide–nitrate systems MCl–MNO_3, MBr–MNO_3.[340–342] The use of halide melts, which are corrosive, made it necessary to modernise the HTMC to prevent the corrosive action of the halides. The inner metallic part of the calorimeter was protected by introducing a glass tube. Since the melting points of the halides are higher than those of the nitrates, the working temperature of the cell was increased to 1100 K,[320] or to ≥1300 K in the study of the fluorides.[343] The measurements were made in an atmosphere of nitrogen[319] or argon.[331] Before the experiment, the salts were placed in a quartz crucible and in a tube with an opening bottom (Fig. 8).

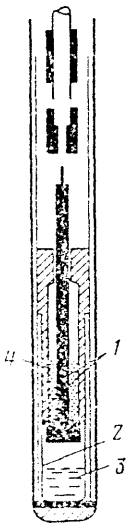


Figure 8. Reaction assembly for measuring the enthalpies of mixing of fluoride melts: *1*) ampoule with opening bottom, *2*) quartz cell, *3*) solvent (melt of the first component), *4*) melt of the second component.

For the study of molten alkali metal fluorides,[343,345] the inner parts of the HTMC were protected more thoroughly against corrosion.[343,344] The calorimeter cell containing the molten fluoride was made of platinum, and the melt of the second fluoride was placed in a platinum tube lowered into the first melt. The melts were mixed by displacing the melt from the tube by a graphite plunger (Fig. 9). This method was used to study the systems MF–M'F,[325,333] MF–MF_2,[344, 346–350] MF–AlF_3,[351,352] MF_2–MF_3,[351,352] MF–MCl, MF–MBr, and MF–MI.[353] The nature of the concentration dependence of the enthalpies of mixing of the fluorides differs from that for other halide systems (Fig. 10); there is considerable deviation from the linear relationship predicted by theory.[348] In the study of various chloride and more particularly fluoride systems, it was assumed that mixing leads to the formation of anionic complexes such as $PbCl_4^{2-}$, $PbCl_5^{3-}$,[329] MgF_4^{2-},[345] BeF_4^{2-}, and AlF_6^{3-}.[345,352]

The enthalpies of mixing have also been studied for oxygen-containing compounds such as carbonates,[354] sulphates,[355] metaphosphates,[160] and hydroxides,[357] and also WO_3(crystalline)–MWO_4(liquid),[358] Cs–CsCl,[359,360] LiF–Na_2SO_4, and Li_2SO_4–NaF.[361] A systematic analysis of experimental data was carried out by Kleppa,[22,342] and the data on binary salt melts was systematised.[363,364]

Thus high-temperature microcalorimetry has led to the accumulation of extensive experimental material with a high reliability. The influence of the size and charge of the ions (cation and anion) on the enthalpies of mixing of binary salt melts has been studied. Fig. 10 gives as an example the dependence of the reduced enthalpy of reaction $[\Delta H/N_1(1 - N_1)]$ on the mole fraction of the component with the smaller ion size.

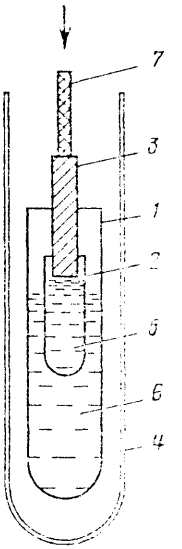


Figure 9. Reaction assembly for measuring the enthalpies of mixing of fluoride melts: *1*) platinum cell, *2*) platinum ampoule, *3*) graphite plunger, *4*) quartz cell, *5*, *6*) fluoride melts, *7*) plunger holder.

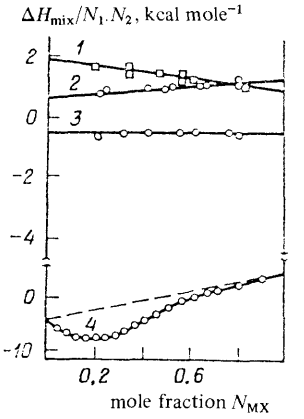


Figure 10. Dependence of the reduced enthalpy of reaction ($\Delta H/N_1.N_2$, kcal mole^{-1}) on the mole fraction (N_1) of the component with the smaller cation: *1*) LiCl–$PbCl_2$, *2*) LiBr–AgBr, *3*) $SrCl_2$–$BaCl_2$, *4*) LiF–BeF_2; N_1 is the mole fraction of the halide (MX) with the smaller cation, where X = chloride, bromide, or fluoride.

VIII. HIGH-TEMPERATURE ENTHALPIES AND ENTHALPIES OF PHASE TRANSFORMATIONS, DETERMINED BY MIXING

The high-temperature enthalpy of a chemical compound, mineral, or metal is determined by the classical thermochemical method of mixing calorimetry[365,366] by dropping a specimen with a mass of up to 20 g, heated in a furnace to the required temperature T, into a calorimeter cell at a constant standard temperature (298 K). The magnitude of the effect is determined by comparing with the values of the differences $H_T - H_{298}$ for standard substances (α-Al_2O_3, Pt, MgO, Au), used to calibrate the instrument.[135,367,368] This method is used to obtain the temperature dependence of $H_T - H_{298}$, and differentiation of this relationship with respect to T gives the temperature dependence of the mean heat capacity. When measurements are made by this method (hot → cold), sudden cooling (quenching) of the specimen is possible, and this may lead to the formation of metastable phases or structural defects and hence to errors which are eliminated only by additional measurments using other methods of study.

Cases of this kind were analysed in a study of the temperature dependence of the heat capacity of lithium ferrite,[348] where it was shown that the published values of $H_T - H_{298}$ for lithium ferrite, obtained by the classical method of mixing calorimetry, may contain a systematic error associated with the quenching of the specimen when it is dropped into the calorimeter cell.

In high temperature microcalorimetry, the specimen at the standard temperature of 298 K is dropped into the microcalorimeter cell heated to the required temperature T, after which the heat used to raise the temperature of the specimen is measured.[78,349] Thus in high-temperature microcalorimetry, the procedure (cold → hot) is the opposite of that in classical mixing calorimetry. High-temperature microcalorimetry makes it possible to eliminate the errors noted earlier. Another advantage of this method is the possibility of using specimens with a comparatively small mass (<1 g), thanks to the high sensitivity of the thermal detectors. The mass of the specimen is usually 100–300 mg.

Table 16. Coefficients of the Mayer–Kelley equation for lanthanide molybdates and ferrites[373,243,233,234,378,379] ($H_T - H_{298} = AT + BT^2 + CT^{-1} + D$).

Compound	A	$10^3 B$	$10^{-5} C$	D
$La_2(MoO_4)_3$	48.06	37.65	8.99	14 645
$Pr_2(MoO_4)_3$	87.14	15.93	25.27	35 846
$Nd_2(MoO_4)_3$	72.96	21.73	8.99	26 696
$Sm_2(MoO_4)_3$	66.91	23.64	−1.57	21 607
$Eu_2(MoO_4)_3$	74.89	22.60	9.00	27 386
$Gd_2(MoO_4)_3$	80.86	12.70	8.77	28 172
$Tb_2(MoO_4)_3$	71.00	18.55	1.87	23 340
$Dy_2(MoO_4)_3$	103.20	26.38	30.97	41 348
$Ho_2(MoO_4)_3$	81.60	12.99	9.00	28 543
$Er_2(MoO_4)_3$	52.02	32.21	−7.00	160 020
$Yb_2(MoO_4)_3$	83.55	97.70	8.99	28 821
$Lu_2(MoO_4)_3$	56.85	28.14	−3.00	18 367
$Y_2(MoO_4)_3$	85.34	53.06	9.00	28 949
$Sc_2(MoO_4)_3$	83.14	79.79	8.58	28 416
$LaFeO_3$	23.18	5.96	0.65	7 655
$PrFeO_3$	19.05	10.42	0.39	6 733
$NdFeO_3$	18.95	9.85	−0.74	6 275
$SmFeO_3$*	18.60	10.84	−0.53	6 328
$EuFeO_3$*	17.84	10.54	−2.37	5 457
$YFeO_3$	20.39	7.57	−1.29	6 316
$LuFeO_3$	22.45	5.47	−1.45	6 689
$Eu_3Fe_5O_{12}$**	32.56	61.32	−32.71	6 258
$Eu_3Fe_5O_{12}$**	129.3	0	0	42 930
$NaLa(MoO_4)_2$	41.21	51.63	7.008	10 260
$NaPr(MoO_4)_2$	269.39	24.76	0.5526	7 454
$NaNd(MoO_4)_2$	−7.643	−25.40	0.3137	—
$NaSm(MoO_4)_2$	−1.220	23.18	0.2928	2 680
$NaEu(MoO_4)_2$	58.58	54.88	0.6239	16 810
$NaGd(MoO_4)_2$	17.03	7.876	0.4517	5 993
$NaDy(MoO_4)_2$	40.40	48.27	0.6615	10 060
$NaHo(MoO_4)_2$	42.20	48.88	0.6541	10 530
$NaEr(MoO_4)_2$	42.62	41.02	0.5975	12 000
$NaYb(MoO_4)_2$	76.74	10.61	0.9620	17 480
$NaLu(MoO_4)_2$	40.42	39.63	0.6009	11 190
$NaY(MoO_4)_2$	69.41	85.99	0.8096	16 390
$NaSc(MoO_4)_2$	4.403	−18.26	0.3068	3 990
$Na_3La(MoO_4)_4$	−1.221	−23.18	0.2923	2 681
$Na_2Mo_2O_7$	89.89	129.48	1.0756	19 596
$Na_2Mo_4O_{13}$	−354.2	−72.20	−39.16	−55 000

*Temperature range 298–915 K. **298–573 K in the first row, 573–975 K in the second row, other compounds 298–973 K.

Table 17. Coefficients of the Mayer–Kelley equation for the high-temperature enthalpies of chemical compounds and minerals, and their heat capacities (C_p, cal mole^{-1} K^{-1}).

Compound	Coefficients of the Mayer–Kelley equation					T, K	Refs.
	A	B	C	D	C_p		
$Ca_3Al_2(SiO_4)_3$ (grossular)	92.02	16.03	17.29	34 658	82	298–1000	[382]
$Ca_3Fe_2(SiO_4)_3$ (andradite)	97.42	12.51	18.73	3 643	86	298–1100	[382]
$Mg_3Al_2(SiO_4)_3$ (pyrope)	87.51	16.38	18.63	33 796	76	298–1100	[382]
$KAl_3Si_3O_{10}(OH)_2$ (muscovite)	101.0	11.6	30.83	41 484	73.2	298–900	[384]
$KMg_3AlSi_3O_{10}(OH)_2$ (phlogopite)	106.03	13.39	24.75	41 103	86.2	298–1100	[384]
$K(MgFe_2)AlSi_3O_{10}(OHF)$ (biotite)	120.35	7.79	33.34	47 422	85.3	298–700	[384]
$Ca_2FeAlSi_3O_{12}(OH)$ (epidote)	113.78	7.35	28.92	44 276	85.6	298–1100	[385]
$Ca_2Fe_{0.3}Al_{2.7}Si_3O_{12}(OH)$ (clinozoisite)	120.18	3.86	33.01	47 248	85.3	298–1100	[385]
$Ca_2Al_2Si_3O_{12}(OH)$ (zoisite)	118.9	4.4	31.5	4 606	86.1	298–1100	[385, 384]
$Mg_7Al_{18}Si_3O_{40}$ (sapphirine)	184.75	9.46	55.4	74 509	128.4	298–1000	[188]
$CaBSiO_4(OH)$ (datolite)	−90.12	26.8	11.15	—	33.66	298–973	[386]
$CaB_2Si_2O_8$ (danburite)	12.26	34.22	22.88	—	—	298–973	[386]
β-BN	7.67	1.74	4.73	4030	—	298–1100	[389]
$NaBeF_3$(liquid)	43 100	160.8	—	—	—	298–1025	[349]
$NaBeF_3$(crystalline)	13 900	9.3	—	—	—	298–1025	[349]
β-Na_2BeF_4(crystalline)	84 100	237.3	—	—	—	448–593	[349]
α-Na_2BeF_4(crystalline)	46 200	155.0	—	—	—	298–448	[349]
γ-Na_2BeF_4(crystalline)	52 300	191.8	—	—	—	593–863	[349]
Na_2BeF_4	83 900	255.8	—	—	—	863–1025	[349]

Table 18. High-temperature enthalpies and enthalpies of phase transformations (kcal mole^{-1}).

Compound	$H_T - H_{298}$; ΔH^0_T	T, K	Refs.
SiO_2 (quartz)	10.46	298–968	[86]
SiO_2 (coesite)	11.65	298–1072	[86]
α-PbO_2	6.233	298–657	[86]
α-PbO_2	6.454	298–599	[86]
TiO_2 (rutile)	10.953	294–965	[390]
GeO_2	10.624+0.015	295–966	[408]
$Li_2Ti_3O_7$	49.87	300–1000	[390]
$Li_{4/3}Ti_{5/3}O_4$	26.97	300–1000	[390]
$La_{0.95}Ca_{0.05}CrO_3$	19.92±0.19	346–938	[376]
$Y_{0.85}Ca_{0.15}CrO_3$	14.72±0.15	382–885	[376]
$CuCr_2S_4$	29.2±0.5	298–975	[380]
$FeCr_2S_4$	29.1±0.5	298–975	[380]
$CoCr_2S_4$	28.7±0.5	298–975	[380]
$NaVO_3$	24.53	298–923	[403]
$CaMgB_2O_5$	30.4±0.4	298–973	[401]
$LiNO_3$ (crystalline-liquid)	5.964±0.083	527	[402]
$NaNO_3$(crystalline-liquid)	3.696±0.032	583	[402]
KNO_3 (crystalline-liquid)	2.413±0.028	610	[402]
$PbNO_3$(crystalline-liquid)	1.105±0.010	589	[402]
$CsNO_3$ (crystalline-liquid)	3.213±0.043	690	[402]
$AgNO_3$(crystalline-liquid)	2.886±0.008	483	[402]
$TlNO_3$(crystalline-liquid)	2.264±0.036	479.5	[402]
$CoTiO_3$*	−1.66±1.02	298	[391]

*Defect spinel–ilmenite phase transformation.

The mixing method using HTMC began to be widely used after the publication of the first studies[86,370] and the development of an automatic device for dropping the specimens.[87] The accuracy of the results obtained by this method is higher when a compact specimen (crystal or tablet) is used. Powdered specimens are placed in a special ampoule made of Pt or Ag, and the heat capacity of the ampoule should not be greater than 15% of the total heat capacity of the specimen and the ampoule.

The improvement of the experimental procedure has made it possible to carry out measurements with extremely small specimen masses (2–10 mg) in the range 400–1100 K;[371,372] the use of a special device (see Fig. 1*b*) led to a marked increase in the sensitivity of the measurements. The heat-absorption time was decreased by a factor of 2, from 70 s to 25–30 s. When the temperature of the HTMC block is kept constant to within ±0.1 K, the uncertainty of the measurements is 2%.

As a consequence of these advantages, the method involving mixing using HTMC has been widely used, for example to determine the temperature dependence of the enthalpy and heat capacity of simple and double molybdates of the lanthanides and yttrium,[243–245,373–375] yttrium and lanthanum chromites,[376,377] yttrium and lathanide ferrites,[233,378,379] double sulphides of chromium, iron, cobalt, and copper,[283,380] quartz,[86] borosilicate and aluminosilicate minerals,[381,386] and a number of other substances and minerals.[40,162,349,387–392] The results of the experimental measurements, treated using the Mayer–Kelley equation and also using a special programme,[393] are given in Tables 16–18.

The method of mixing using HTMC also make it possible to study the energies of the transformations taking place when the dropped specimen is heated. Thus the enthalpy of the volatilisation of MoO_3 was measured by dropping MoO_3 (298 K) into an HTMC cell heated to 1086.1 K and 1119.4 K [373] and weighing after keeping for different time intervals; a similar method was used to determine the enthalpy of fusion of $NaBeF_3$.[349] The method of mixing from 298 K to 1083 K [391] was used to study the enthalpy of the defect spinel–ilmenite transformation in a $CoTiO_3$ specimen, and the phase transformation in TiO_2.[396] Most studies, however, have been devoted to the sublimation, volatilisation, or fusion of metals, for example the study of the enthalpy of the sublimation of zinc and tellurium at 1093 K [397,398] and of cadmium at 590 K;[399] an extremely large amount of experimental data has been obtained, and it cannot be examined in the present review.

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While the present review was being prepared for publication, new papers appeared on the study of the theory[411] and practice[412,413,414] of high-temperature microcalorimetry, the thermochemical properties of lanthanide oxides, manganese borides, iron and aluminium vanadates, alkali metal perrhenates, lanthanide tungstates, and ferrite solid solutions,[415–420] and also on the thermochemistry of minerals.[421–423]

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Geology Department
Lomonosov Moscow State University
Mendeleev Moscow Institute
of Chemical Technology,
Moscow

Translated from *Uspekhi Khimii*, 53, 1463-1492 (1984) U.D.C. 546.39'161

The Properties and Reactions of Ammonium Fluorides

E.G.Rakov and E.I.Mel'nichenko

The most important thermal properties of ammonium fluorides and fluorometallates, and the reactions of ammonium fluorides with elements, other simple fluorides, oxides, and salts have been reviewed.
The bibliography contains 379 references.

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I. INTRODUCTION

Inorganic fluorides play an important role in modern technology. The principal methods for their preparation are based on the use of anhydrous hydrogen fluoride, fluorine, and hydrofluoric acid, and, on a smaller scale, halogen fluorides.[1] The original raw materials for the production of all these reagents are fluorite concentrates, which are treated with sulphuric acid to give hydrogen fluoride or hydrofluoric acid; hydrogen fluoride is decomposed electrolytically to give fluorine, and fluorine is used to synthesise halogen fluorides.[2]

This is not the only scheme, however. Phosphorite and apatite concentrates, which are raw materials for the phosphorus fertiliser industry,[3] are used in addition to fluorite concentrates as an industrial source of fluorine on every scale. A technical by-product (ammonium "fluoride–hydrogen fluoride"), consisting of a mixture of NH_4HF_2 and NH_4F, is now being obtained from the waste gases from the production of superphosphates.[4–8] Pure and technical grade ammonium fluorides can be used to obtain anhydrous hydrogen fluoride and hydrofluoric acid, and also directly for fluorination. They have been used, for example, to extract metals from beryl,[9] ilmenite,[10] pyrochlore,[11] monazite,[12] and scheelite,[13–15] to dissolve metals,[16] to purify fluorides,[17] and to obtain the fluorides of aluminium,[18] zinc,[19] cadmium,[20] and many other metals.

As a result of the exhaustion of rich fluorite deposits, the increase in the production of phosphoric acid and phosphorus fertilisers, and the need to obtain more complete utilisation of fluorine compounds, the volume of fluorides obtained from natural phosphorites, and the importance of ammonium fluorides as fluorinating agents, are increasing continuously.

Ammonium fluorides (anhydrous or in aqueous solution) react with many substances. These reactions are specific, and are accompanied by the formation of ammonium fluorometallates or oxofluorometallates. Increase in the temperature of synthesis or the action of heat on the fluorometallates lead to their thermal decomposition. The characteristic regular features of these reactions and the thermal properties of fluorometallates are important for optimising the conditions for the synthesis of fluorides using ammonium fluorides. Since published data on these topics have not been summarised before, the aim of the present review was to fill this gap.

A special section of the review is devoted to a brief description of the properties of ammonium fluorides, since these properties to a large extent determine the thermal characteristics of ammonium fluorometallates,[21] and it is necessary to supplement the last review, published about 10 years ago.[22]

II. PROPERTIES OF AMMONIUM FLUORIDES

Two compounds of ammonia with hydrogen fluoride, stable under ordinary conditions, are known: NH_4F and NH_4HF_2.

Ammonium fluoride is a colourless substance which forms hexagonal crystals with the wurtzite lattice (space group $P6mc$).[23–27] This distinguishes it from other ammonium halides, which have cubic structures, and is related to the formation of strong hydrogen bonds by NH_4F [28] and is responsible for the fact that the NH_4^+ groups are immobile in the crystal.[29,30] At 23°, the crystal lattice of NH_4F has the parameters: $a = 0.4439$ nm, $c = 0.7165$ nm, $z = 2$.[23,31] The measured and calculated values of the density are 1.002 g cm^{-3} and 1.006 g cm^{-3} respectively.[31]

The boiling point of NH_4F is not known. When heated, NH_4F decomposes according to the equation

$$2\,NH_4F(\text{crystalline}) \rightarrow NH_4HF_2(\text{crystalline}) + NH_3(\text{gas}) \qquad (1)$$

and this also distinguishes it from other ammonium halides. In the temperature range 343–383 K, the decomposition pressure (the equilibrium pressure of the gaseous products) is given by the expression[32]

$$\lg p\,[\text{mmHg}] = -8.82996 + 3022.966/T + 6.87415 \lg T$$

and in the range 404.2–438.9 K it is given by the equation:[33]

$$\lg p\,[\text{mmHg}] = 47.863 - 6582/T - 11.365 \lg T$$

The temperature at which the NH_3 pressure becomes equal to 760 mmHg is ~167 °C.[33–35]

The standard enthalpy of reaction (1), determined calorimetrically, is 19.7 kcal, and the value calculated from tensimetric data is 19.1 kcal.[36] The enthalpy of the reaction

$$NH_4F(\text{crystalline}) \rightarrow NH_3(\text{gas}) + HF(\text{gas})$$

at 298 K is 35.8 ± 0.9 kcal (calorimetry) or 35.1 ± 1.0 kcal (tensimetry).[36] The standard enthalpy of formation of NH_4F [37] is 110.8 ± 0.6 kcal mole^{-1}, and the Gibbs free energy $\Delta G^0_{\text{formation}}$ (298 K, NH_4F, crystalline) = −83.28 kcal mole^{-1}. The values were obtained assuming that $\Delta H^0_{\text{formation}}$ (298 K, HF, gas) = −64.8 kcal mole^{-1}, although the absolute value accepted at present is larger (−65.32 kcal mole^{-1}).[38]

The standard heat capacity and entropy of crystalline NH_4F are 15.60 ± 0.02 cal mole^{-1} K^{-1} and 17.20 ± 0.05 cal mole^{-1} K^{-1}.[39] The heat capacity data in Ref.40 do not agree with those in Ref.39, and are apparently erroneous.

Ammonium fluoride is readily soluble in water; its solubility at 25 ° is 45.38%.[41] It is unstable in aqueous solution, and when heated it decomposes with the liberation of NH_3, so that it cannot be obtained by evaporating its solutions;[4,6,7,41] NH_4F is readily soluble in liquid HF, and with NH_4HF_2 it forms a eutectic melting at 109.3°.[35,43]

Ammonium hydrogen fluoride (bifluoride) is a colourless slightly hygroscopic substance, which forms an orthorhombic crystal lattice with parameters $a = 0.840$, $b = 0.816$, $c = 0.367$ nm, $z = 4$, space group *Pman*, calculated density 1.505 g cm^{-3}.[23] The NH_4^+ group is joined to the F atom by hydrogen bonds: each fluorine atom forms two hydrogen bonds with nitrogen atoms, and one with another fluorine atom.[44] The melting point of NH_4HF_2 is 126.45°, and the enthalpy of fusion 4.564 ± 0.002 kcal mole^{-1}.[45]

The decomposition pressure of solid NH_4HF_2 at 343–383 K is given by the equation:[32]

$$\lg p\ [\text{mmHg}] = 5.42446 - 3424.363/T + 1.60995 \lg T$$

Over a wider temperature range (209–399.3 K), the decomposition pressure is given by the expression:[33]

$$\lg p\ [\text{mmHg}] = 6.723 - 3295/T + 6.915 \lg T - 0.00547\,T.$$

The decomposition pressure of liquid NH_4HF_2 in the range 392.5–411.7 K is given by the equation:[33]

$$\lg p\ [\text{mmHg}] = 20.809 - 4256/T - 3.6 \lg T + 0.00028\,T$$

The boiling point of NH_4HF_2 is ~238 °C.[6,7,33,35,46] Liquid NH_4HF_2 has an anomalously high compressibility, compared with the solid phase.[47]

The standard enthalpy of the reaction

$$NH_4HF_2(\text{crystalline}) \rightarrow NH_3(\text{gas}) + 2HF(\text{gas})$$

is 51.9 ± 0.2 kcal mole^{-1} [36] or 51.4 kcal mole^{-1} [48] from calorimetric data, or 51.1 kcal mole^{-1} [32,36] from tensimetric data. In Ref. 37, the value of $\Delta H^0_{\text{formation}}$ (298 K, NH_4HF_2, crystalline) was taken as −191 ± 1 kcal mole^{-1}. From calorimetric data, C_p^0(298 K) = 25.48 cal mole^{-1} K^{-1}, and S^0(298 K) = 27.61 cal mole^{-1} K^{-1}.[23,37,49]

Ammonium hydrogen fluoride is readily soluble in water. At 25° its solubility is 41.50 mass %[41] or 41.08 mass %,[48] and the enthalpy of solution to give a saturated solution is 5.12 ± 0.06 kcal mole^{-1}.[48] The soluion is accompanied by the absorption of heat. The density of the saturated solution at 25° is 1.1273 g cm^{-3}.[50] NH_4HF_2 is also readily soluble in liquid HF. In the NH_4HF_2–HF system, the compounds $NH_4H_3F_4$ and $NH_4H_5F_6$, which melt congruently (melting points 23.2° and −8.0°) and decompose readily with the liberation of HF, are formed.[43]

Thus ammonium hydrogen fluoride is of greatest interest as a fluorinating agent. Ammonium fluoride, when heated to medium temperatures, decomposes to ammonium hydrogen fluoride, and at temperatures above 165–170° it can exist only at an ammonia pressure greater than 1 atm. The "vapours" of ammonium fluorides, that is their thermal decomposition products, contain hydrogen fluoride, and can therefore take part in reactions characteristic of HF.

The properties of ammonium fluorides are such that in the thermal decomposition of ammonium fluorometallates, in addition to the absorption of heat as a result of decomposition to simple fluorides, at temperatures above 165–170° (and more particularly above 235–240°) absorption of heat takes place as a result of the highly endothermic decomposition of ammonium fluoride itself.

III. THERMAL PROPERTIES OF AMMONIUM FLUORO- AND OXOFLUOROMETALLATES

All the transition elements except the heavy actinides, and also beryllium, magnesium, and the non-transition elements of groups III–V except carbon and nitrogen, can form ammonium fluorometallates. Transition elements from the central part of the periodic system (mainly metals of groups V–VII), and also uranium and the non-transition elements of group V, also form oxofluorometallates.

Subsequent sections examine the compositions of the compounds and give the sequence of stages in the thermal decomposition, the temperatures of the separate stages, and the enthalpies of formation and other thermodynamic parameters of ammonium fluoro- and oxofluorometallates, except for the characteristics of the low-temperature phase transformations.

1. Compounds of Non-Transition Elements

Beryllium forms $(NH_4)_2BeF_4$, NH_4BeF_4, and $NH_4Be_2F_5$.[51–53] The tetrafluoroberyllate decomposes with the successive formation of NH_4BeF_3, $NH_4Be_2F_5$, and BeF_2; the minima of the endothermic effects on the differential thermal analysis (DTA) curves for the first two stages lie at 300° and 360°;[53] under isothermal conditions, the decomposition can be carried out at lower temperatures.[52] The standard enthalpy of formation of $(NH_4)_2BeF_4$ is −475.7 ± 1.5 kcal mole^{-1},[54,55] the Gibbs free energy $\Delta G^0_{\text{formation}} = 413.1$ kcal mole^{-1},[55] $S^0 = 59.8 \pm 0.6$ cal mole^{-1} K^{-1}, and $C_p^0 = 50.4 \pm 0.5$ cal mole^{-1} K^{-1}.[55,56]

Magnesium forms $MgF_2.2NH_4F.2H_2O$, $MgF_2.2NH_4F$, and $MgF_2.NH_4F$. Dehydration takes place at 110°;[57] $MgF_2.2NH_4F$ decomposes to $MgF_2.NH_4F$ and then to MgF_2 at 215–220° and 280–285° respectively.[57–59]

The fluoroborates NH_4BF_4 and $NH_4BF_4.NH_4F$,[60] and a large number of oxofluoro- and hydroxofluoroborates, for example $NH_4B(OH)_2F_2$, $NH_4B(OH)_3F$, NH_4BOF_4 or $(NH_4)_3B_3O_3F_{12}$, $(NH_4)_2BOF_3$, $(NH_4)_2B_3O_3(OH)F_4$, and $(NH_4)_2B_4OF_{12}$,[61,62] have been synthesised.

The thermogram of ammonium tetrafluoroborate shows endothermic effects with minima at 176 and 346°, corresponding to its polymorphic transformation and decomposition (sublimation).[61] According to Refs. 63 and 64, the temperature of the transformation is 205 ± 3°, and according to Ref. 65 it is 208 ± 2°. The enthalpy of the transformation is 2.4 ± 0.1 kcal mole^{-1}.[65] The decomposition pressure is given by the equation[66]

$$\lg p\ [\text{mmHg}] = 6.82 - 2469/T$$

so that the decomposition temperature is close to 354°, and the enthalpy of decomposition is close to 33.9 kcal mole^{-1}. The standard values of C_p^0 and S^0 for NH_4BF_4 are 32.09 cal mole^{-1} K^{-1} and 46.77 cal mole^{-1} K^{-1}.[67] According to Refs. 65 and 66 and the estimates of the present authors, $\Delta H^0_{\text{formation}}$ (298 K, NH_4BF_4, crysallline) ≦ −381.4 kcal mole^{-1}, $\Delta G^0_{\text{formation}}$ (298 K, NH_4BF_4, crystalline) ≦ −341 kcal mole^{-1}.

The reaction

$$(NH_4)_2B_3O_3(OH)F_4 \rightarrow NH_4BF_4 + B_2O_3 + NH_3 + H_2O$$

takes place at 200–250°.[68]

Aluminium, gallium and indium form higher fluorometallates with the same composition, $(NH_4)_3MF_6$. The hexafluoroaluminate decomposes in two stages with the successive formation of NH_4AlF_4 and γ-AlF_3.[69,72] It has been reported[7] that the thermal decomposition also gives the compound $NH_4AL_2F_7$, and

the compound $(NH_4)_2HAlF_6.H_2O$ has been described in a patent.[73]

The reactions

$$(NH_4)_3AlF_6(\text{crystalline}) \rightarrow NH_4AlF_4(\text{crystalline}) + 2NH_3(\text{gas}) + 2HF(\text{gas})$$
$$NH_4AlF_4(\text{crystalline}) \rightarrow \gamma\text{-}AlF_3 + NH_3(\text{gas}) + HF(\text{gas})$$

give endothermic effects at 305° and 450°; the equilibrium constants of these reactions are given by the equations:[71,72]

$$\lg K_p = 30.455 - 18182/T \quad (507 \leqslant T \leqslant 578\ \text{K})$$
$$\lg K_p = 17.240 - 13071/T \quad (663 \leqslant T \leqslant 731\ \text{K})$$

The mean enthalpies of decomposition of $(NH_4)_3AlF_6$ and NH_4AlF_4 are 83 ± 1 kcal mole^{-1} and 60 ± 1 kcal mole^{-1}, and the enthalpies of formation −731.3 kcal mole^{-1} and −496.6 kcal mole^{-1} respectively.[64]

According to Refs.74 and 75, $(NH_4)_2GaF_5.H_2O$ is dehydrated at 100–150°, and decomposes with the successive removal of two NH_4F molecules at 350° and 450°. Ammonium hexafluoroindate is converted at 280° into the pentafluoroindate, which then decomposes in two stages at 320° and 400°.[76] In Ref.77, much lower temperatures are given for the start of the separate stages (120, 170, and 185°). These data are less accurate, since if NH_4F were removed at such low temperatures, the thermograms would also have shown the effect at 238° corresponding to the "boiling" of NH_4HF_2. $(NH_4)_5In_3F_{14}$, $NH_4In_2F_7$, and $NH_4In_3F_{10}$ have been obtained directly from the simple fluorides.[78] $(NH_4)_2Ga(OH)_2F_3$ and $(NH_4)_2In(OH)_2F_3$ have also been described.[79]

Silicon forms the double salt $(NH_4)_2SiF_6.NH_4F$, which according to thermographic data decompose above 190°, and also ammonium hexafluorosilicate, which decompose above 300°.[80,81] The vapour pressure over $(NH_4)_2SiF_6$ at 532–592 K is given by the equation:[81]

$$\lg p\ [\text{mmHg}] = 9.94 - 4170/T$$

If it is assumed that $(NH_4)_2SiF_6$ decomposes to SiF_4, NH_3, and HF, the values of the enthalpies of decomposition and formation of $(NH_4)_2SiF_6$ from the elements are 95.4 kcal mole^{-1} and −633.1 kcal mole^{-1} respectively. The standard enthalpy of formation, determined calorimetrically, is −642.6 kcal mole^{-1}, the Gibbs free energy is −567.4 kcal mole^{-1}, $S^0 = 68.0$ cal mole^{-1} K^{-1}, and $C_p^0 = 59.25$ cal mole^{-1} K^{-1}.[82,83]

Germanium forms compounds similar to the silicon compounds: $(NH_4)_2GeF_6.NH_4F$ and $(NH_4)_2GeF_4$.[64] The hexafluorogermanate decomposes in a single stage with a minimum on the DTA curve at 400°.[85]

Tin(II) forms the fluorostannate $(NH_4)_2SnF_4.2H_2O$,[86] described as early as 1886, and also NH_4SnF_3 and $NH_4Sn_2F_5$.[87] The last two compounds decompose in an evacuated vessel at 160–200°.

Tin(IV) forms the fluorides $(NH_4)_4SnF_8$, $(NH_4)_2SnF_6$ (described in 1859),[86] $(NH_4)_2SnF_6.NH_4F$, $(NH_4)_2Sn(OH)F_5$, $(NH_4)_2Sn(OH)_2F_4.H_2O$, $(NH_4)_4Sn_2OF_{10}$, and $(NH_4)_3HSn_2OF_{10}$.[88] The thermal decomposition of $(NH_4)_2SnF_6.NH_4F$ takes place at 320°, and $(NH_4)_2SnF_6$ decomposes in two stages, at 410° and 500°[85] (according to Ref.89, the hexafluorostannate(IV) decomposes at 210°). The hydroxofluorostannates(II) decompose in three stages in the range 80–360°.[88]

Phosphorus(V) forms the fluoro-acids hexafluorophosphoric acid HPF_6, difluorophosphoric acid HPO_2F_2, and monofluorophosphoric acid H_2PO_3F, all of which form ammonium salts;[86] $NH_4PF_6.NH_4F$ has also been described.[90] Ammonium difluorophosphate and monofluorophosphate are thermally stable at 135°; the monofluorophosphate decomposes at 220° to NH_4HPO_3F, which melts at ~226°.[91,92]

Arsenic(V) gives similar compounds: NH_4AsF_6,[93] $NH_4As.(OH)F_5$, $NH_4As(OH)_2F_4$,[94] and $(NH_4)_2AsO_2F_2$.[95]

Antimony(III) gives the following compounds with alkali metal and ammonium cations: M_2SbF_5, $MSbF_4$, MSb_2F_7, and MSb_4F_{13};[96,97] *antimony(V)* forms M_2SbF_7 and $MSbF_6$. The compound $(NH_4)_2SbF_5$ undergoes phase transformations at temperatures between −23° and 17°.[98]

Bismuth(III) forms NH_4BiF_4.[86]

The melting point of NH_4SO_3F is 245°.[96]

2. Compounds of the Transition Elements

Copper(II) forms the compounds $(NH_4)_2CuF_4$ and NH_4CuF_3, which separate from aqueous solutions as the hydrates,[86] but which can also be obtained anhydrous.[99] The decomposition of NH_4CuF_3 gives a minimum on the DTA curve at 250°, and is accompanied by the absorption of 34.2 kcal mole^{-1}.[100]

Zinc and cadmium form the fluorides $(NH_4)_2ZnF_4.2H_2O$, $(NH_4)_2CdF_4.2H_2O$,[101] NH_4ZnF_3, NH_4CdF_3;[99,100] the anhydrous fluorides $(NH_4)_2CdF_4$ and $(NH_4)_3Cd_2F_7$ have also been described.[102] The decomposition temperatures of the trifluorometallates of zinc and cadmium are 250° and 205°, and the enthalpies of decomposition are 33.9 kcal mole^{-1} and 33.3 kcal mole^{-1} respectively.[100] As in the case of the fluorocuprate, the values obtained for the enthalpy of decomposition are lower than the value for the decomposition of NH_4F itself, so that they must be regarded with caution.

Scandium forms complex compounds with compositions corresponding to those of the aluminium compounds. Ammonium hexafluoroscandate decomposes at 260–290° and 340–350° with the successive formation of NH_4ScF_4 and ScF_3.[103–105]

The equilibria for the reactions

$$(NH_4)_3ScF_6(\text{crystalline}) \rightarrow NH_4ScF_4(\text{crystalline}) + 2NH_3(\text{gas}) + 2HF(\text{gas})$$
$$NH_4ScF_4(\text{crystalline}) \rightarrow ScF_3(\text{crystalline}) + NH_3(\text{gas}) + HF(\text{gas})$$

at 448–492 K and 563–605 K respectively are described by the equations:[106]

$$\lg K_p = 29.8 - 15400/T$$
$$\lg K_p = 16.0 - 10200/T$$

The mean enthalpies of decomposition of $(NH_4)_3ScF_6$ and NH_4ScF_4 are 70.5 kcal mole^{-1} and 46.7 kcal mole^{-1} respectively. Since they are independent of temperature, and $\Delta H^0_{\text{formation}}(298\ \text{K}, ScF_3, \text{crystalline}) = -394 \pm 2$ kcal mole^{-1},[107] the standard enthalpies of formation of the corresponding ammonium fluoroscandates can be found (−737 ± 7 kcal mole^{-1} and −517 ± 5 kcal mole^{-1}).

Yttrium forms the compound $NH_4Y_2F_7.NH_4F$, which decomposes in two stages, at 260° and 380°, to give $NH_4Y_2F_7$ and YF_3.[106] The equilibrium for the reaction

$$NH_4Y_2F_7(\text{crystalline}) \rightarrow 2YF_3(\text{crystalline}) + NH_3(\text{gas}) + HF(\text{gas})$$

at 601–653 K is described by the equation:

$$\lg K_p = 12.9 - 9000/T$$

Thus the mean enthalpy of decomposition is ~41 kcal mole^{-1}.

In the systems LnF_3–NH_4F–H_2O (Ln = lanthanum or a lanthanide), crystalline phases with the most varied compositions have been detected.[108,109] The compounds identified

most reliably are $(NH_4)_3LnF_6$, $(NH_4)_3Ln_2F_9$, NH_4LnF_4 (or $(NH_4Ln_2F_7.NH_4F)$, and $NH_4Ln_2F_7$.[110–114] According to Ref. 110, many lanthanides also form the compounds $(NH_4)_3Ln_2F_9.H_2O$. La, Pr, Nd, Sm, Eu, Gd, and Tb form tetrafluorometallates NH_4LnF_4, which decompose directly to LnF_3; Dy, Ho, Er, Tm, Yb, and Lu form $NH_4Ln_2F_7.NH_4F$ or $(NH_4)_3.Ln_2F_9$, which decompose at 250–270° to $NH_4Ln_2F_7$, and at 350° to LnF_3.[110,111]

Table 1. Characteristics of the decomposition of NH_4LnF_4.

Ln	T, K	$\lg K_p = A - B/T$		ΔH_T^0, kcal mole^{-1}
		A	B	
Pr	478—516	18.556	9 980	45.6
Nd	478—523	18.551	10 201	46.7
Sm	500—528	17.070	9 780	44.7
Gd	497—545	19.150	10 858	49.7

The decomposition pressures and enthalpies of decomposition of various Ln compounds are given in Table 1.[111]

The equilibrium for the reaction

$$NH_4Dy_2F_7(\text{crystalline}) \rightarrow 2DyF_3(\text{crystalline}) + NH_3(\text{gas}) + HF(\text{gas})$$

at 584–614 K is described by the expression:

$$\lg K_p = 32.003 - 20122/T$$

The enthalpy of the reaction is 46.0 kcal mole^{-1}.[111]

The thermal decomposition of NH_4EuF_4 takes place at 258° with the absorption of 21.8 ± 0.1 kcal mole^{-1}.[114] The enthalpy of the process was found in Ref.114 by differential scanning calorimetry, and is apparently too low.

The compounds $(NH_4)_3Ln_2F_9.H_2O$, where Ln = La, Pr, Sm, and Er, are dehydrated at 100°, and then decompose to $NH_4Ln_2F_7$ (at 200–215° for Sm and Eu) or to NH_4LnF_4 (at 170–185° for La and Pr). For the La Salt, the dehydration and the removal of NH_4F take place simultaneously.[109] According to Ref.109, the compounds $(NH_4)_2Ln_3F_{11}.H_2O$, where Ln = Dy, Ho, and Er, also exist, and at 60–120° decompose to $(NH_4)_2Ln_3F_{11}$ and then to $NH_4Ln_3F_{10}$ (at 204° for Ho) or to the trifluorides (at 159° for Dy and at 316° for Er). These data are apparently contradictory. For example, it is not clear why the trifluoride is formed from $(NH_4)_3Dy_2F_7$ at temperatures above 350°, but is formed from $NH_4Dy_3F_{10}$ even at 159°.

According to Ref.113, $(NH_4)_3NdF_6$ decomposes to NH_4NdF_4 at 350–400° and to NdF_3 at ~500°. The decomposition of $(NH_4)_3Ce_2F_9$ at 430° in a vacuum leads to the successive formation of NH_4CeF_4 and CeF_3.[115] According to Ref.116, NH_4CeF_4 decomposes to CeF_3 at 400–450°.

Cerium is unique among the lanthanides in its ability to form Ce^{IV} compounds. $(NH_4)_4CeF_8$, $(NH_4)_3CeF_7$, $(NH_4)_2CeF_6$, NH_4CeF_5, and $(NH_4)_7Ce_6F_{31}$ are known.[117–119] The decomposition of the most complex compounds begins at 108°, and is complete at 430° with the formation of CeF_3. Anhydrous CeF_4 may be formed at 300°.[118]

The actinides(IV) Th, Pa, U, Np, Pu, and Am have properties similar to those of Ce^{IV}. For each of these elements, the most complex ammonium fluorometallates are $(NH_4)_4AnF_8$ (where An = actinide), which decompose successively to $(NH_4)_2AnF_6$, $NH_4Th_2F_9$, $NH_4Th_2F_9.H_2O$,[125] and $7NH_4F.2ThF_4.H_2O$.[126]

Thorium forms $(NH_4)_4ThF_8$, which gives slightly different decomposition products. $(NH_4)_3ThF_7$,[124] $(NH_4)_2ThF_6$, $NH_4Th_2F_9$, $NH_4Th_2F_9.H_2O$,[125] and $7NH_4F.2ThF_4.H_2O$ [126] have been described.

Uranium forms the fluorometallate series $UF_6.nNH_4F$, $UF_5.nNH_4F$, and $UF_4.nNH_4F$. Ammonium oxofluorouranates(VI), or ammonium uranyl fluorides, are also known.

Only one ammonium fluorouranate(VI) has been obtained: NH_4UF_7.[124–126] According to Ref.127, its thermal decomposition takes place in three stages, involving the exothermic reduction of U^{VI} to U^V at 100–130°, the decomposition of NH_4F at 200–320°, and reduction to UF_4 at 350–450°. NH_4UF_6 is formed in the first stage.[128]

The UF_5–NH_4F system gives $(NH_4)_3UF_8$, $(NH_4)_2UF_7$, and NH_4UF_6.[128,129] According to Ref.130, the last compound is stable in a vacuum at 150°, although in Refs.131 and 132, vigorous exothermic decomposition is reported. In Ref.131, the mechanism of the decomposition was described by the equation

$$NH_4UF_6 \rightarrow UF_4 + NH_4F + 1/2\,F_2$$

which has not been rigorously proved, however, since fluorine and NH_4F are incompatible (see section IV).

U^{IV} compounds have been most extensively studied. Studies of the system UF_4–NH_4F and UF_4–NH_4F–H_2O [121,133,134] have made it possible to characterise $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, $7NH_4F.6UF_4$, NH_4UF_5, and $NH_4F.3UF_4$. The reported[135] existence of anhydrous $(NH_4)_3UF_7$, $NH_4U_2F_9$, $NH_4U_4F_{17}$, and $NH_4U_6F_{25}$ is not sufficiently well-founded.

The octafluorouranate(IV) is stable in air to ~100°,[121] the hexafluorouranate(IV) to 225–250°, the pentafluorouranate(IV) to 350°, and $NH_4F.3UF_4$ to 450°.[136] In a vacuum, $(NH_4)_2UF_6$, NH_4UF_5, and $NH_4F.3UF_4$ decompose at 180, 290, and 400°.[121] The reported formation of HUF_5 from NH_4UF_5 at 320–360° [137] has not been confirmed.

The enthalpies of formation of $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, $7NH_4F.6UF_4$, and $NH_4F.3UF_4$ are −941 ± 4, −413 ± 20, and −1510 ± 10 kcal mole^{-1}. The results[138] were calculated using the most reliable value for the standard enthalpy of formation of UF_4.[107]

The estimated values of the Gibbs free energy of formation of the compounds, given in Ref.119, are inaccurate. According to more reliable data,[139] for the formation of $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, and $7NH_4F.6UF_4$ from the simple crystalline fluorides, the values of the change in the Gibbs free energy are −23.5, −20.9, and −97.1 kcal mole^{-1} respectively.

In the systems UO_2F_2–NH_4F–H_2O [140,141] and UO_3–NH_4F–H_2O,[142,143] the most stable complex compound is $(NH_4)_3UO_2F_5$. Its thermal decomposition takes place in two stages

$$(NH_4)_3UO_2F_5(\text{crystalline}) \rightarrow 1/2\,NH_4(UO_2)_2F_5(\text{crystalline}) + 5/2\,NH_3(\text{gas}) + 5/2\,HF(\text{gas})$$

$$1/2\,NH_4(UO_2)_2F_5(\text{crystalline}) \rightarrow UO_2F_2(\text{crystalline}) + 1/2\,NH_3(\text{gas}) + 1/2\,HF(\text{gas})$$

and the decomposition pressures are given by the equations:[144]

$$\lg p,\ [\text{atm}] = 8.01 - 4468/T \quad (516 \leqslant T \leqslant 558\ \text{K})$$

$$\lg p,\ [\text{atm}] = 6.927 - 4878/T \quad (647 \leqslant T \leqslant 703\ \text{K})$$

The mean enthalpies of decomposition are 102 ± 3 kcal mole^{-1} and 22 ± 2 kcal mole^{-1}.

The enthalpies of formation of $(NH_4)_3UO_2F_5$ and $NH_4.(UO_2)_2F_5$, found from tensimetric data,[144] are −749.4 kcal mole^{-1} and −918.0 kcal mole^{-1}, and coincide with the

calorimetric data (−748.9 ± 2.2 kcal mole^{-1} and −921.5 ± 2.8 kcal mole^{-1} from Refs.107 and 145, or −753 kcal mole^{-1} and −919 kcal mole^{-1} from Ref.138). The above values of the enthalpies of formation of oxofluorouranates(VI) were refined slightly by the present authors using published data[107] for UO_2F_2.

Under certain strictly defined conditions, ammonium oxofluorouranates(VI) can apparently sublime, and this has been made the basis of a method for extracting uranium from its ores.[146] These conditions cannot be determined from the thermal characteristics of salts and UO_2F_2 available at present.[147]

The hydrate $NH_4(UO_2)_2F_5.4H_2O$ melts at 64.5° and decomposes to give the trihydrate, which melts at 98.7° and decomposes to the anhydrous salt.[141] The enthalpies of formation of the hydrates have been measured.[148]

The data in Ref.149 on the formation of $NH_4UO_2F_3$ have not been confirmed experimentally by other workers, and are unreliable; the existence of an exothermic effect in the decomposition of pure $NH_4(UO_2)_2F_5$ [150] appears unlikely.

Neptunium forms fluorometallates in which the oxidation state of the metal is +4,[122] although the existence of neptunium(V) compounds is possible. The thermal decomposition begins at ~120° for $(NH_4)_4NpF_8$, 220° for $(NH_4)_2NpF_6$, 280° for $7NH_4F.6NpF_4$, and 300° for NH_4NpF_5. The most stable compound (up to ~600–650°) is $NH_3Np_3F_{13}$, which decomposes to the tetrafluoride.

Plutonium fluorides have properties similar to those of uranium fluorides. The thermal decomposition of ammonium octafluoroplutonate(IV) in air at 160° gives the hexafluoroplutonate, and at 210° the compound $7NH_4F.6PuF_4$; the latter is converted into NH_4PuF_5 in oxygen at 220°, into $NH_4F.3PuF_4$ in a vacuum at 290°, and into PuF_4 in a vacuum at 330°.[121] The formation of PuF_4 in the decomposition of ammonium fluoroplutonates(IV) has been confirmed;[151,152] the hydrate $NH_4PuF_5.2H_2O$ was not detected. Other workers,[119,153], however, report that the decomposition is complete with the formation of plutonium trifluoride. PuF_4 can apparently be reduced by ammonia, and the composition of the final product depends on the thermal decomposition conditions.

Published data[154] indicate that the thermal decomposition of ammonium fluorocurates(IV) also gives the trifluoride.

The transition metals of group IV in the oxidation state +4 do not form such a wide variety of fluorometallates as the actinides.

Titanium(IV) forms the compounds $(NH_4)_2TiF_6.NH_4F$,[155,156] $(NH_4)_2TiF_6$,[157] and NH_4TiF_5,[158] the first two of which were described in the middle of the last century by Marignac. Their decomposition in an inert medium is accompanied by the transfer of titanium to the gas phase (to the extent of 75% from published thermogravimetric curves,[85] 85% according to Ref.157, more than 95% according to Ref.158, and 100% according to Ref.159). The differences in the values obtained are due to differences in the moisture content of the gases surrounding the specimens, and the tendency of fluorotitanates to undergo hydrolysis.[160–162] Ammonium heptafluorotitanate decomposes slowly at temperatures above 150°, the hexafluorotitanate above 250°, and the pentafluorotitanate above 280°.

The enthalpy of formation of $(NH_4)_2TiF_6$ from the simple crystalline fluorides at 25° is −30.0 ± 1.0 kcal mole^{-1},[163] and that from the elements (using published data[164] for TiF_4) is −645.8 ± 2.6 kcal mole^{-1}.

Ammonium oxofluorotitanate $(NH_4)_2TiOF_4$,[158] peroxofluorotitanate $(NH_4)_3Ti(O_2)F_5$,[163,166] and fluorotitanate(III) NH_4TiF_4 also exist. The last compound decomposes to non-volatile titanium trifluoride at 600° in a stream of Ar or H_2.[167]

Zirconium(IV) and hafnium(IV) form $(NH_4)_3MF_7$, $(NH_4)_2MF_6$, and NH_4MF_5, whose thermal decomposition has been studied in detail.[157,168–173] The DTA curves show endothermic effects with minima at 315, 365, and 435° for $(NH_4)_3ZrF_7$, and at 300, 360, and 430° for $(NH_4)_3HfF_7$. Each minimum corresponds to the removal of 1 mole of ammonium fluoride. The equilibrium values of the decomposition pressures and enthalpies of decomposition of the zirconium and hafnium compounds are given in Table 2.

Table 2. Characteristics of the decomposition of Zr and Hf salts.[172]

Reactions	T, K	$\lg K_p = A - B/T$		ΔH^0_T, kcal mole^{-1}
		A	B	
3:1 → 2:1	525–567	13.79	8 330	38.1
2:1 → 1:1	578–625	12.72	8 500	38.8
1:1 → ZrF_4	640–687	14.42	10 500	48.1
3:1 → 2:1	518–565	16.28	8 710	44.4
2:1 → 1:1	578–625	14.60	9 750	44.6
1:1 → HfF_4	630–688	18.85	11 270	51.5

Note. 3 : 1, 2 : 1, and 1 : 1 represent respectively the formulae $(NH_4)_3MF_7$, $(NH_4)_2MF_6$, and MH_4MF_5, where M = Zr or Hf.

The enthalpies of the successive addition of crystalline NH_4F to crystallise ZrF_4, found from these values, are −12.9, −3.6, and 3.0 kcal mole^{-1}, which show satisfactory agreement with the calorimetric data (−13.5, −5.4, and −0.9 kcal mole^{-1}).[174] Thus the standard enthalpies of formation of $(NH_4)_3ZrF_7$, $(NH_4)_2ZrF_6$, and NH_4ZrF_5 −809.2 ± 0.7, −697.5 ± 0.7, and −581.2 ± 0.7 kcal mole^{-1} respectively. The Gibbs free energies are −703.6, −619.0, and −529.9 kcal mole^{-1} respectively (the absolute values of these quantities given in Ref. 164 are lower by ~5 kcal mole^{-1}).

For hafnium, the mean enthalpies of the successive addition of NH_4F to the tetrafluoride are −16.8, −9.4, and −8.6 kcal mole^{-1},[172] and the enthalpies of formation of $(NH_4)_3HfF_7$, $(NH_4)_2HfF_6$, and NH_4HfF_5 are −829.2, −709.6, and −589.2 kcal mole^{-1} respectively.

The enthalpy of the phase transformation of $(NH_4)_2ZrF_6$ at 138 °C is 1.7 kcal mole^{-1},[174,175] and the enthalpies of the transformations of $(NH_4)_2HfF_6$ at 140 °C and 240 °C are −1.39 kcal mole^{-1} and 1.18 kcal mole^{-1}.[175] The existence of the transformations influences the kinetics of the thermal decomposition.[173] The hydrate $NH_2ZrF_5.H_2O$ is also known; its standard enthalpy of formation is −651.97 ± 0.6 kcal mole^{-1}.[176]

The transition elements of group V have three characteristic oxidation states: +5, +4, and +3, so that in principle they can form compounds of the series $MF_5.nNH_4F$, $MOF_3.nNH_4F$, $MO_2F.nNH_4F$, $MF_4.nNH_4F$, $MOF_2.nNH_4F$, and $MF_3.nNH_4F$.

Vanadium forms compounds of all the series except $VF_4.nNH_4F$. Ammonium hexafluorovanadate(V) is very hygroscopic, and apparently thermally unstable.[177] Ammonium dioxotetrafluorovanadate is extremely unstable, and decomposes even at 50–60°. When this compound is heated,

$(NH_4)_2VO_2F_3$ is formed at 140°, $(NH_4)_3V_2O_4F_5$ at 160°, and $NH_4VO_2F_2$ at 180°.[178] The last compound begins to decompose at 150°[179] to give first an unidentified oxofluorovanadate, and then at 360° an oxide fluoride in which the oxidation state of vanadium is lower than +5[178] (the decomposition in air is complete with the formation of a product which does not contain fluorine).[180]

According to Ref.85, the oxofluorovanadate(IV) $(NH_4)_3VOF_5$ decomposes to give $(NH_4)_2VOF_4$, NH_4VOF_3, and VOF_2 successively at 250–300, 320–360, and 390–430°. The compound $NH_4V_3O_6F$ is also known;[181] the thermal decomposition of $(NH_4)_3VF_6$ begins at 250°, passes through stages involving the formation of $(NH_4)_2VF_5$, $VF_3.0.3NH_4F$, and VF_3, containing 0.1–1.5% NH_4^+, and is complete at 650–700° with the formation of the trifluoride.[182]

Niobium forms only ammonium oxofluoroniobates(V). The thermal decomposition of $(NH_4)_3NbOF_6$ gives $(NH_4)_2NbOF_5$, NH_4NbOF_4, and NbO_2F successively at 255, 320, and 420°.[183] It was also suggested[183] that the decomposition of NH_4NbOF_4 gives the oxide fluoride $NbOF_3$, which then decomposes to NbO_2F and NbF_5.

The most complex ammonium fluorometallate formed by tantalum is $(NH_4)_3TaF_8$, which is unstable even at 100°.[184] The more stable $(NH_4)_2TaF_7$ decomposes at 310° and 390° to give NH_4TaF_6, and then a mixture of TaF_5, NH_3, and HF.[184] The presence of water vapour leads to hydrolysis to TaO_2F and to a decrease in the quantity of tantalum volatilised. The enthalpies of formation of $(NH_4)_2TaF_7$ from the crystalline fluorides and from the elements at 298.15 K are −31.4 kcal mole^{-1} and −708.1 ± 0.4 kcal mole^{-1} respectively.[185]

According to Ref.183, the course of the thermal decomposition of $(NH_4)_3TaOF_6$ is similar to that described above for niobium, except that the separate stages take place at 175, 290, and 465°. It was suggested[183] that crystalline $TaOF_3$ exists in the temperature range 320–465°, but this appears unlikely, since attempts by other workers to isolate this compound have been unsuccessful. Heating moist NH_4TaOF_4 in air at 1000° gives mainly Ta_2O_5.[186] More complex oxofluoroniobates and oxofluorotantalates have also been isolated.[183]

Chromium forms NH_4CrO_3F,[187,188] $(NH_4)_3CrF_6$, $(NH_4)_2CrF_5.2H_2O$,[189,190] and NH_4CrF_4.[191] Ammines of chromium trifluoride are also known.[192]

Molybdenum forms the compounds NH_4MoF_7,[124,193,194] $NH_4Mo_2F_{13}$,[194] NH_4MoF_6, NH_4MoF_5, $(NH_4HF_2)_2MoF_5$,[196] NH_4MoOF_5,[194] $6NH_4F.7MoOF_4$,[195] $(NH_4)_3MoO_2F_5$, $(NH_4)_2MoO_2F_4$, $NH_4MoO_2F_3$,[196–199] $(NH_4)_3MoO_3F_3$, and $(NH_4)_2MoO_3F_2$.[200–201] The properties of many of the compounds have been reviewed.[202]

NH_4MoF_7 decomposes at 70, 145, and 380° according to the scheme:[203]

$$NH_4MoF_7 \rightarrow NH_4MoF_6 \rightarrow NH_4MoF_5 + MoF_5 + NH_4F \rightarrow MoF_3 + Mo_2N_3$$

The compound $6NH_4F.7MoOF_4$ (and probably NH_4MoOF_5) is stable up to 190°, although the most intense endothermic effect on the DTA curve is observed at 420°;[195] its decomposition products were not identified. The salt $(NH_4)_3MoO_2F_5$ is unstable, and decomposes even at 90–115° to give $(NH_4)_2.MoO_2F_4$; the latter is converted into $NH_4MoO_2F_3$ at 210° to 230°,[196] and at temperatures above 270–300° into a non-volatile molybdenum oxide fluoride containing 64.2% Mo, 10.9% F, and 2.0% N.[204]

Data on the thermal decomposition of $(NH_4)_2MoO_3F_2$ and $(NH_4)_3MoO_3F_3$ indicate that they have a high thermal stability; the first compound decomposes at 375°, and the second at 300°.[202]

Tungsten forms fewer ammonium fluorometallates than molybdenum. NH_4WF_7,[124] $(NH_4)_3WO_2F_5$, $(NH_4)_2WO_2F_4$, $(NH_4)_3W_2O_4F_7$,[197,198] $(NH_4)_3WO_3F_3$, $(NH_4)_2WO_3F_2$, $9NH_4F.5WO_3$, and NH_4WO_3F[205] have been characterised.

The thermal decomposition of $(NH_4)_3WO_2F_5$ gives $(NH_4)_2.WO_2F_4$, $(NH_4)_3W_2O_4F_7$, and $NH_4W_2O_2F_7$ successively at 240, 285, and 330°. The last compound decomposes at 380° to give an oxide fluoride, which was first assigned the composition WOF_2,[197,198] and then $W_2O_4F.n(N_mOF)$.[204,206] It is most probably an oxide fluoride bronze AW_2O_4F, in which the inserted cations A are NH_4^+, H_3O^+, and H_2F^+.[207]

Ammonium peroxofluoromolybdates(VI) and peroxofluorotungstates(VI) are also known.[208,209]

Manganese forms the fluorides $(NH_4)_3MnF_6$, $(NH_4)_2MnF_5$, and NH_4MnF_4,[210–212] and also NH_4MnF_3.[100] When heated, $(NH_4)_3MnF_3$ gives endothermic effects at 92, 115, and 203°. The last of these is due to decomposition to $(NH_4)_2MnF_5$, which in turn decomposes at 240–285° and 305–320° to NH_4MnF_4 and MNF_2. NH_4MnF_3 decomposes at 310° with the absorption of 38.5 ± 0.5 kcal mole^{-1}.[100]

Technetium and rhenium form the compounds $(NH_4)_2MF_6$, which decompose in an inert medium or in a vacuum at 300°.[213] The formation of nitride fluorides in the decomposition, postulated in Ref.213, was refuted by other workers.[214]

Stable compounds are formed by iron in two oxidation states: +3 and +2. The thermal decomposition of $(NH_4)_3FeF_6$ gives NH_4FeF_6 at 280°, and iron trifluoride at 410°.[69] In addition, the appearance of phases with the composition $(NH_4)_xFeF_{3+x}$, where x = 0.7–0.8 and 0.1–0.2, has been observed. The standard heat capacity of $(NH_4)_3FeF_6$ is 70.5 ± 1.7 cal mole^{-1} K^{-1}.[215]

The composition of ammonium hexafluoroferrate(III), isolated from aqueous solutions, does not correspond to the traditionally accepted formula. According to Ref.216, this compound has the composition $(NH_4)_{2.6}FeF_{5.6}.0.4H_2O$. The thermal properties of NH_4FeF_3[217,318] have not been studied. The existence of $NH_4Fe^{2+}Fe^{3+}F_6$ is possible.

The decomposition of $(NH_4)_2CoF_4$ gives an endothermic effect at 260°.[219] The NH_4CoF_3 formed decomposes at 290,[100] 310,[192] of 335°[219] to give CoF_2. The enthalpy of decomposition of NH_4CoF_3 is 30.4 ± 0.5 kcal mole^{-1}.[100]

Nickel forms the compounds $(NH_4)_2NiF_4$[219,220] and NH_4NiF_3. The first compound decomposes at 270°,[219] and the second at 290°[100] or 370°.[219] The enthalpy of decomposition of NH_4NiF_3 is 35.0 ± 0.5 kcal mole^{-1}.[100]

IV. REACTIONS OF AMMONIUM FLUORIDES

1. Reactions with Elements

The reactions with many elements can be described by the following equations:

$$E + nHF(gas) \rightarrow EF_n(crystalline) + \frac{n}{2}H_2 \quad (2)$$

$$E + \frac{n}{2}NH_4HF_2(crystalline) \rightarrow EF_n(crystalline) + \frac{n}{2}H_2 + \frac{n}{2}NH_3 \quad (3)$$

$$E + nNH_4F(crystalline) \rightarrow EF_n(crystalline) + \frac{n}{2}H_2 + nNH_3 \quad (4)$$

Table 3 shows that each of these reactions is probable for the alkali and alkaline earth metals, and also beryllium.

When the products are not simple fluorides, but fluorometallates, for example ammonium fluoroberyllates, the absolute values of ΔG^0 for the reactions are greater than those characteristic of reactions (2)–(4). The most negative values are observed for the reaction of a mixture of gaseous NH_3 and HF.

Table 3. Gibbs free energies ($-\Delta G^0$, kcal mole^{-1} for reactions (2)–(4) for non-transition elements of groups I and II (at 298 K).[23,55]

Reaction	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba
(2)	75.4	65.0	65.3	59.8	60.3	103.5	125.4	149.9	146.8	141.9
(3)	65.2	58.8	53.3	49.6	50.1	83.1	105.0	129.5	126.4	121.5
(4)	61.3	50.9	49.4	45.7	46.2	75.3	97.2	124.7	118.6	109.8

The results of the calculations given in Table 3 are confirmed by experimental data. Metallic beryllium is readily soluble in aqueous NH_4F solutions, and the rate of solution has the values 0.6 mg cm^{-2} min^{-1} and 2.4 mg cm^{-2} min^{-1} at 50° and 97°.[221] NH_4F solutions can be used to remove the beryllium coverings of fuel elements, and for the selective solution of beryllium from UBe_{13} alloy.[222]

With increase in the group number, the probability of reactions (2)–(4) for non-transition elements decreases (Table 4).

Carbon should obviously be inert with respect to all the reagents examined; phosphorus is probably stable to ammonium fluorides; arsenic and the group VI elements should also be inert.

Aluminium and silicon give high negative values of the Gibbs free energy. The formation of ammonium hexa- and tetrafluoroaluminates from a mixture of gaseous HF and NH_3 and crystalline NH_4HF_2 and NH_4F is highly exothermic. This is also true of the reactions

$$Si + 6HF(gas) + 2NH_3(gas) \rightarrow (NH_4)_2SiF_6(crystalline) + 2H_2$$
$$Si + 3NH_4HF_2(crystalline) \rightarrow (NH_4)_2SiF_5(crystalline) + 2H_2 + NH_3(gas)$$
$$Si + 6NH_4F(crystalline) \rightarrow (NH_4)_2SiF_6(crystalline) + 2H_2 + 4NH_3(gas)$$

for which the enthalpies at 298 K are −232, −81, and −22 kcal mole^{-1}, and the Gibbs free energies −168,0, −106.0, and −83.2 kcal mole^{-1}.[23,37,81,83] This explains why exothermic reactions of NH_4HF_2 with aluminium and silicon (at 120° and 80° respectively) were observed.[223] Since aluminium is kinetically relatively stable towards anhydrous HF,[224] NH_4HF_2 apparently dissolves the fluoride film on the metal surface. It is apparently because of these properties that mixtures containing NH_4HF_2 have been recommended for the cleaning and chemical polishing of aluminium and its alloys.[225–227]

Of the non-transition elements of groups VI and VII, oxygen and fluorine react with the ammonia present in ammonium fluorides. These reactions are used to isolate hydrogen fluoride[228,229] or nitrogen trifluoride.[230]

The regular features of the change in the probability of fluorination are slightly different for transition metals. Table 5 shows that reactions (2)–(4) are most probable for the elements of the central part of the periodic system, that is in groups III, IV, and V. Copper, silver, gold, mercury, molybdenum, tungsten, the group VII metals, and the platinum metals should be stable towards HF and ammonium fluorides. The values of ΔG^0 for the formation of Fe, Co, and Ni difluorides are −17.2 −17.8, and −15.3 kcal mole^{-1} respectively for reaction (2), and +11.0, +10.4, and +12.9 kcal mole^{-1} respectively for reaction (4).[23,164]

Table 4. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (2)–(4) for non-transition elements of groups III–VI (at 298 K).

Reaction	B	Al	In	C	Si	Ge	P	As	S	Se	Te
(2)	−71.9	−146.2	−34.1	48.9	−114.9	−13.6	−36.1	46.3	128.1	148.9	99.8
(3)	−41.3	−115.6	−3.5	89.7	−73.8	27.2	14.9	97.3	189.3	201.1	161.0
(4)	−29.6	−103.9	8.2	105.3	−58.2	42.8	34.4	116.8	212.7	233.5	184.4

Note. The calculation was carried out for the higher fluorides, which in all cases except Al and In were gaseous; the data from Refs.23, 37, 83, and 64 were used.

Table 5. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (2)–(4) for transitions elements (at 298 K).

Reaction	Cu^I	Ag^I	Zn	Cd	Hg	Sc	Y	La	Tl	Zr	Hf	V	Nb	Ta	Mo	W
(2)	9	20.4	−39.9	−24.6	42	−179	−197	−199	−111.4	−171.4	−176.2	−2.9	−79.5	−101	39.8	1.0
(3)	19	30.6	−19.5	−4.2	62	−148	−166	−168	−70.6	−130.6	−135.4	48.1	−28.5	−50	101.0	62.2
(4)	23	34.5	−11.7	3.6	70	−137	−155	−157	−55.0	−115.0	−119.8	67.6	−9.0	−31	124.4	85.6

Note. The calculation was carried out for the higher fluorides; the fluorides of V, Mo, and W were assumed to be liquid; the data from Refs.23, 107, and 164 were used.

The reactions of various transition metals may stop at the stage of lower fluoride formation. This is characteristic, for example, of titanium, which forms the trifluoride only on prolonged contact with gaseous HF in the absence of oxidising agents and moisture.[224,231]

The probability of fluorination increases if fluorometallates are formed. For the reaction

$$Zr + 6HF(gas) + 2NH_3(gas) \rightarrow (NH_4)_2ZrF_6(crystalline) + {}^3/_2H_2$$

$$Zr + 3NH_4HF_2(crystalline) \rightarrow (NH_4)_2ZrF_6(crystalline) + {}^3/_2H_2 + NH_3(gas)$$

$$Zr + 6NH_4F(crystalline) \rightarrow (NH_4)_2ZrF_6(crystalline) + {}^3/_2H_2 + 4NH_3(gas)$$

The absolute values of the standard free energies ΔG^0 are greater than those given in Table 5, and are −518, −230, and −135 kcal mole^{-1} (from Ref. 164 with allowance for the corrections described in section III of the present review). Thus the reaction with ammonium fluorides to give fluorometallates is unlikely only for copper, mercury, vanadium, molybdenum, and tungsten. The other transition metals of groups II–V (including scandium, yttrium, lanthanum, the lanthanides, and the actinides), in the absence of kinetic restrictions, can react readily under ordinary conditions with ammonium fluorides to give fluorometallates.

Thus NH_4HF_2 is used to etch zirconium and its alloys,[232] and aqueous NH_4F solutions can be used to dissolve titanium, zirconium, and hafnium.[233]

Niobium and tantalum dissolve in liquid NH_4HF_2 and react with it.[16] The enthalpies of the reactions

$$2M + 5NH_4HF_2(liquid) \rightarrow (NH_4)_2MF_7(crystalline) + 3NH_4F(crystalline) + MH_{0.8}(crystalline) + 2.1H_2$$

$$MH_{0.8}(crystalline) + {}^7/_2NH_4HF_2(liquid) \rightarrow (NH_4)_2MF_7(crystalline) + {}^3/_2NH_3(gas) + 2.9H_2$$

are close to −49 kcal mole^{-1} and −24 kcal mole^{-1} for niobium, and close to −64 kcal mole^{-1} and −54 kcal mole^{-1} for tantalum.[16] Niobium and tantalum react with gaseous hydrogen fluoride to form the pentafluorides,[234,235] so that their reactions with "gaseous" ammonium fluorides are quite problabe.

2. Reactions with Other Simple Fluorides

Many ammonium fluorometallates can be obtained by the direct reaction of the simple fluorides. Thus UF_4 and PuF_4 add on NH_4F at 80–130°,[121] UF_5 at 80–85°,[128,130] $TiOF_2$ at 80°,[158] and UF_6 at room temperature.[125] Stoichiometric mixtures of the simple fluorides have been used to obtain NH_4MgF_3,[58] NH_4CdF_3,[102] NH_4MnF_3,[211] $(NH_4)_2NiF_4$,[220] NH_4CoF_3,[236] and ammonium fluoroindates.[78] Compounds more highly saturated in NH_4F can be obtained by the reaction of the less saturated compounds with NH_4F. Thus heating equimolar mixtures of $(NH_4)_2SiF_6$ or $(NH_4)_2TiF_6$ with NH_4F at 90° to 95° gives the heptafluorometallates.[81,158]

Solid-phase syntheses using NH_4F are generally time-consuming, however (complete reaction takes from several hours to several days), and to avoid the loss of NH_3 and the partial loss of HF they must be carried out in closed vessels. To increase the reaction rates, mixtures of the powdered reagents can be compressed or heated under pressure[236] (liquid NH_4F is an ionic conductor[237]), but it is better to use solvents.

The most widely used solvent is water. The equilibrium solubility in metal fluoride (fluorometallate)–NH_4F–H_2O systems has been studied for BeF_2,[238,239] NH_4BF_4,[60] AlF_3,[240] GaF_3,[74,241] InF_3,[76] TlF,[242,243] $(NH_4)_2SiF_6$,[244] SnF_2,[87] CuF_2,[245] CdF_2,[246] CeF_4,[117] UF_4,[133,134] UO_2F_2,[140–142], CoF_2,[245] and NiF_2.[245] The NH_4BF_4–NH_4HF_2–H_2O system has been studied.[60]

Anhydrous HF,[194,247] ClF_3,[124] methanol,[99] polymerised trifluoroethylene,[248] etc. have also been used as solvents. HF, however, decomposes many fluorometallates, ClF_3 reacts with NH_4F (sometimes explosively) on slight heating, and the solubility of NH_4F in organic solvents is low (in Ref. 125, a suspension of NH_4F in trichloroethylene was used).

Table 6 gives the enthalpies of formation of fluorometallates, and shows that the maximum values of $-\Delta H^0_{formation}$ are observed for $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, $(NH_4)_3AlF_6$, $(NH_4)_3HfF_7$, and $(NH_4)_2SiF_6$. If however the enthalpy is related to 1 mole of NH_4F, it decreases in a slightly different order: NH_4AlF_4, $(NH_4)_2UF_6$, NH_4HfF_5, $(NH_4)_2TaF_7$, $(NH_4)_2TiF_6$, etc., although in this case also the compounds of the elements of groups III–V are among the energetically most stable compounds. Comparison of the enthalpies of addition in the series $MF_n.nNH_4F$–$MF_2.nNH_4F$–$MF_3.nNH_4F$–$MF_4.nNH_4F$–$MF_5.nNH_4F$–$MF_6.nNH_4F$, where M represents a given metal in different oxidation states or metals from the same row of the periodic system, shows that the enthalpy tends first to increase and then to decrease.

Table 6. Enthalpies of formation of fluorometallates (at 298 K).

Substance	$-\Delta H^0_{formation}$, kcal mole^{-1}		Substance	$-\Delta H^0_{formation}$, kcal mole^{-1}	
	I	II		I	II
$(NH_4)_2BeF_4$	8.6	78.6	$(NH_4)_3UF_8$	39	109
NH_4BF_4	−1	33.9	$7NH_4F.6UF_4$	525	770
$(NH_4)_3AlF_6$	38	143	$NH_4F.3UF_4$	9.4	44
NH_4AlF_4	25	60	$(NH_4)_3UO_2F_5$	17.7	122.7
$(NH_4)_2SiF_6$	35	105	$NH_4(UO_2)_2F_5$	13.1	48
NH_4CuF_3	−1	34	$(NH_4)_2TiF_6$	31	101
NH_4ZnF_3	−1	34	$(NH_4)_3ZrF_7$	19.8	125
NH_4CdF_3	−2	33	$(NH_4)_2ZrF_6$	18.9	89
$(NH_4)_3ScF_6$	13	117	NH_4ZrF_5	13.5	48.5
NH_4ScF_4	12	47	$(NH_4)_3HfF_7$	36	141
$NH_4Y_2F_7$	6	41.2	$(NH_4)_2HfF_6$	26	96
NH_4PrF_4	10.6	45.6	NH_4HfF_5	17	51
NH_4NdF_4	11.7	46.7	$(NH_4)_2TaF_7$	31.4	101
NH_4SmF_4	9.7	44.7	NH_4MnF_3	4	39
NH_4GdF_4	14.7	49.7	NH_4CoF_3	−5	30
$NH_4Dy_2F_7$	11	46.0	NH_4NiF_3	0	35
$NH_4)_4UF_8$	40	180			

Note. I) from the simple crystalline fluorides; II) from MF_n(crystalline), HF(gas), and NH_3(gas). For references see Section III.

Fluorometallates with the maximum number of coordinated fluorine atoms have a lower thermal stability and a lower enthalpy of formation from the simple fluorides (calculated for 1 mole of NH_4F) than the compounds of the same metal with a smaller number of added NH_4F molecules.

NH_4HF_2 can also react with simple fluorides to give ammonium fluorometallates. $(NH_4)_2NiF_4$ has been obtained from NiF_2,[249] and $(NH_4)_2NiF_4$ and $(NH_4)_2CoF_4$ from NiF_2 and CoF_2 dihydrates.[219]

The reactions

$$MF_n(crystalline) + mNH_4HF_2(crystalline) \rightarrow (NH_4)_mMF_{n+m}(crystalline) + mHF(gas)$$

take place with a much smaller liberation of heat (by 15.4m kcal mole^{-1})[23] than the reactions

$$MF_n(crystalline) + mNH_4F(crystalline) \rightarrow (NH_4)_mMF_{n+m}(crystalline)$$

The difference in the Gibbs free energies for the reactions of NH_4HF_2 and NH_4F is smaller, and amounts to 8.8m kcal mole^{-1}. At the same time, the values of ΔH^0 and ΔG^0 for the

reactions of "gaseous" NH_4F and NH_4HF_2 should not be different. Thus the reactions

$$\underbrace{MF_n + mNH_3(gas) + 2mHF(gas)}_{\text{vapour over } NH_4HF_2} \rightarrow (NH_4)_mMF_{n+m}(\text{crystalline}) + mHF(gas)$$

can be used to obtain hydrogen fluoride from NH_4HF_2. This method was first patented by Sudarikov and co-workers;[250] silicon tetrafluoride is used, and the reaction is carried out at 140° with liquid NH_4HF_2 or at 200° with "gaseous" NH_4HF_2. A wider range of fluorides is listed in other patents,[251–253] which mention, in particular, the fluorides of copper, magnesium, calcium, zinc, aluminium, indium, thorium, germanium, tin, titanium, zirconium, vanadium, bismuth, chromium, iron, and nickel, and also fluorometallates not saturated in NH_4F. The preferred temperature range for carrying out the reactions is 125–200°.

Processes for obtaining hydrogen fluoride, based on the formation and thermal decomposition of alkali metal hydrogen fluorides, are of much greater practical importance. Usually, an aqueous solution of NH_4F and the sodium salt is heated to give $NaHF_2$, which is filtered off, dried, and heated. Ammonia, the mother-liquor, and sodium fluoride are returned to the same or another stage of the process. Sodium hydrogen fluoride can also be obtained by the reaction of anhydrous NH_4HF_2 and NaF, which begins at 105°.[254] Different versions of the method have been described and patented;[255–263] it can also be applied to potassium salts.[275, 264–267]

Ammonium hydrogen fluoride forms compounds and mixed crystals with the alkali metal hydrogen fluorides.[268–270]

The reaction of gaseous SiF_4 with NH_4F solution has been proposed for preparing $(NH_4)_2SiF_6$[271] and for trapping SiF_4 from gas streams.[4,8,272]

3. Reactions with Oxides and Hydroxides

Reactions with oxides and hydroxides, which are widely encountered in nature and are involved in many technological processes, are of considerable practical importance.

For the hydroxides of the alkali and alkaline earth elements (and also Be and Mg), the following reactions are of interest:

$$M(OH)_n(\text{crystalline}) + nHF(gas) \rightarrow MF_n(\text{crystalline}) + nH_2O(gas) \quad (5)$$

$$M(OH)_n(\text{crystalline}) + \frac{n}{2}NH_4HF_2(\text{crystalline}) \rightarrow MF_n(\text{crystalline}) + nH_2O(gas) + \frac{n}{2}NH_3(gas) \quad (6)$$

$$M(OH)_n(\text{crystalline}) + nNH_4F(\text{crystalline}) \rightarrow MF_n(\text{crystalline}) + nH_2O(gas) + nNH_3(gas) \quad (7)$$

The final products for the alkali metal hydroxides can apparently be hydrogen fluorides:

$$MOH(\text{crystalline}) + 2HF(gas) \rightarrow MHF_2(\text{crystalline}) + H_2O(gas) \quad (8)$$

$$MOH(\text{crystalline}) + NH_4HF_2(\text{crystalline}) \rightarrow MHF_2(\text{crystalline}) + H_2O(gas) + NH_3(gas) \quad (9)$$

$$MOH(\text{crystalline}) + 2NH_4F(\text{crystalline}) \rightarrow MHF_2(\text{crystalline}) + H_2O(gas) + 2NH_3(gas) \quad (10)$$

Table 7 shows that all these processes are probable. The same is true of many reactions involving the fluorination of oxides:

$$MO_{n/2}(\text{crystalline}) + nHF(gas) \rightarrow MF_n(\text{crystalline}) + \frac{n}{2}H_2O(gas) \quad (11)$$

$$MO_{n/2}(\text{crystalline}) + \frac{n}{2}NH_4HF_2(\text{crystalline}) \rightarrow MF_n(\text{crystalline}) + \frac{n}{2}H_2O(gas) + \frac{n}{2}NH_3(gas) \quad (12)$$

$$MO_{n/2}(\text{crystalline}) + nNH_4F(\text{crystalline}) \rightarrow MF_n(\text{crystalline}) + \frac{n}{2}H_2O(gas) + nNH_3(gas) \quad (13)$$

Table 7. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (5)–(7) for non-transition elements of groups I and II and for reactions (8)–(10) for the alkali metals (at 298 K).

Reaction	Li	Na	K	Be	Mg	Ca	Sr	Ba
(5)	−24.4	−28.1	−27.2	−18.3	−35.5	−43.4	−48.5	−46.1
(6)	−14.2	−17.9	−17.0	2.1	−15.1	−23.0	−28.1	−25.7
(7)	−10.3	−14.0	−13.1	9.9	−7.3	−15.2	−20.3	−14.9
(8)	−26.5	−26.8	−28.8	—	—	—	—	—
(9)	−6.0	−6.3	−8.3	—	—	—	—	—
(10)	1.7	1.4	−0.6	—	—	—	—	—

Note. The data from Refs. 23, 55, and 273 were used in the calculation.

Table 8. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (11)–(13) for non-transition elements of groups II–VI (at 298 K).

Reaction	Be	Mg	Ca	Sr	Ba	B	Al	C	Si	Ge	P	As	S
(11)	−19.7	−44.1	−59.1	−69.5	−71.5	−11.1	−138.9	33.8	−19.2	1.8	−13.5	1.3	40.9
(12)	0.7	−23.7	−38.7	−49.1	−51.1	20.6	−107.1	74.8	21.8	42.8	37.8	52.6	102.4
(13)	8.5	−15.9	−30.9	−41.3	−40.3	31.2	−96.6	90.2	37.2	58.2	57.0	71.8	125.5

Note. The calculation was carried out for the higher oxides and fluorides; the latter, for B, C, Si, Ge, P, As, and S were gaseous; the data from Refs. 23, 37, 64, 83, and 274 were used.

The data in Table 8 show that the reactions of the oxides of all non-transition elements of group II are probable. The higher oxides of the non-transition elements of groups III–V, except carbon, can react with HF to form higher fluorides, but with increase in the group number, the values of ΔG^0 for the reactions become more positive, and the reactions become less probable.

In many cases, the fluorination is characterised by larger absolute negative ΔG^0 values or smaller absolute positive ΔG^0 values, because of fluorometallate formation. Thus the reactions of α-quartz with crystalline NH_4HF_2 and NH_4F to give $(NH_4)_2SiF_6$ take place with $\Delta G^0 = -10.8$ kcal mole^{-1} and +12.3 kcal mole^{-1}.[83] There is also a high probability that oxide fluorides, and not fluorides, will be formed. For example, the values of ΔG^0 for the fluorination of P_2O_5 (crystalline) and SO_3 (gas) to gaseous POF_3 and SO_2F_2 are −18.5 kcal mole^{-1} and −29.5 kcal mole^{-1}.[23,37,274]

Many processes have been well studied by experimental methods. Thus BeO and moist $Be(OH)_2$ react with NH_4HF_2 on heating to 50–100°.[52,80,275] Different versions of the fluorination of alkali and alkaline earth metal oxides have been described.[276–281]

The fluorination of boric acid by anhydrous ammonium fluorides or their aqueous solutions gives NH_4BF_4,[61,62,65,282–284] but with a deficit of fluorinating agent and a short contact time the products are mixtures of $(NH_4)_2BOF_3$, $(NH_4)_3B_3O_3F_6$, and other ammonium oxo- and hydroxofluoroborates.[61,62,68,285]

A detailed study[286] showed that the reactions of $Al(OH)_3$ and Al_2O_3 with NH_4HF_2 begin at 20–130°, take place with considerable liberation of heat, and give $(NH_4)_3AlF_6$. Increase in the alumina heating temperature from 500° to 1200°, leads to a sharp decrease in its activity: a specimen obtained at 1200° is inert towards NH_4HF_2. Different versions of the process have been described.[287–291]

The reaction in a mixture of SiO_2 and NH_4HF_2 begins at a temperature of ~100° and takes place exothermally to give $(NH_4)_2SiF_6.NH_4F$.[80,81] Quartz dissolves relatively rapidly in aqueous NH_4HF_2 solutions.[292] Ammonium fluorides and their solutions have therefore been recommended for the removal of oxides from semiconductor surfaces[293] and for the removal of quartz from fluorite concentrates.[294–299] Silica is also soluble in alkaline and neutral NH_4F solutions,[300,301] and the rate of solution on heating is relatively high.[302] NH_4F solutions at 150–400° can be used for the hydrothermal preparation of single crystals of quartz and amethyst.[303]

The reaction of P_2O_5 with NH_4HF_2 or NH_4F takes place rapidly at 135° with the liberation of a large quantity of heat, to give $NH_4PO_2F_2$ or $(NH_4)_2PO_3F$.[91,304,305] Heating As_2O_3 with concentrated NH_4HF_2 solution for 1 h gives NH_4AsO_2.[94]

Table 9 shows that the regular features of the change in ΔG^0 for the fluorination of higher oxides to fluorides are slightly different for the transition elements than for non-transition elements. With increase in the group number, the probability of fluorination at first increases, reaching a maximum for the group III elements, and then decreases. In this case also, the reaction products for the metals of group V and VI may be oxide fluorides or ammonium oxofluorometallates, and this may lead to a considerable change in the ΔG^0 values.

Ammonium fluoride and more particularly ammonium hydrogen fluoride are fairly powerful fluorinating agents for many transition metal oxides. Thus ZnO reacts rapidly with molten NH_4HF_2 [278] or its "vapour" at 300°.[19]

The reaction of Sc_2O_3 with NH_4HF_2 begins at 60°, takes place with exothermic and endothermic effects, and is complete at 180° with the formation of $(NH_4)_3ScF_6$.[306] Y_2O_3 is fluorinated by ammonium hydrogen fluoride with an exothermic effect at 80° and an endothermic effect at 170°.[106,307,308] With an excess of NH_4HF_2, the initial product is $NH_4Y_2F_7.NH_4F$, which decomposes to YF_3. With a deficit of the fluorinating agent, yttrium oxide fluoride is formed.[309,310] It has also been suggested that the fluorination involves the formation of ammines of the trifluoride in intermediate stages.[309,310]

The fluorination is similar for La_2O_3, which is converted into NH_4LaF_4 or $NH_4La_2F_7$,[110,112,114] but which may also give the oxide fluoride or ammine.[309,310] The oxides of all the lanthanides are fluorinated with an exothermic effect at 80–180°; Eu_2O_3 is converted into NH_4EuF_4.[114] It has been concluded[110,112] that for Pr, Nd, Sm, and Gd, the first stage of the reaction gives the compounds NH_4LnF_4. According to Ref.111, Dy_2O_3 is first converted into $NH_4Dy_2F_7$, and according to Refs.110 and 112, the oxides of Dy, Ho, Er, Tm, Yb, and Lu give the compounds $(NH_4)_3Ln_2F_9$ in the initial stages of the fluorination. With a relatively small quantity of NH_4HF_2 at temperatures of 300–360°, hexagonal oxide fluorides were detected[111] in the fluorination products of the oxides of Pr, Nd, Sm, and Gd.

Table 9. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (11)–(13) for transition element (at 298 K).

Reaction	Cu^{II}	Ag^{I}	Zn	Cd	Hg	Sc	Y	La
(11)	−9.7	−9.5	−17.9	−24.4	1.0	−43.9	−62.0	−77.3
(12)	10.7	4.7	2.5	−4.0	21.4	−13.3	−31.4	−46.7
(13)	18.5	8.6	10.3	3.8	29.3	−1.6	−19.7	−35.0
	Tl	Zr	Hf	V	Nb	Ta	Mo	W
(11)	2.7	−31.4	−31.9	21.1	−15.2	−19.5	35.6	19.8
(12)	43.5	9.4	9.1	72.1	35.8	31.5	96.8	81.0
(13)	59.1	25.0	24.5	91.6	55.3	51.0	120.2	104.4

Note. The calculation was carried out for the higher oxides and fluorides; the latter, for V, Mo, and W, were liquid; the data from Refs.23 and 107 were used.

The fluorination of CeO_2 gives $(NH_4)_3CeF_7$ at 60° [117,118] and $(NH_4)_{0.6}CeF_{4.45}$ at 200°.[115]

NH_4F solutions at 200–300° can be used for the hydrothermal synthesis of single crystals of ammonium fluorometallates of erbium.[311]

The oxides of the light actinides (thorium, uranium, neptunium, plutonium, americium, and, apparently, protactinium) are fluorinated by ammonium fluoride or ammonium hydrogen fluoride at relatively low temperatures. Thus the conversion of $Th(OH)_4$ into ThF_4 by the action of NH_4F,[12] the fluorination of NpO_2,[122] the fluorination of PuO_2,[151–153] and the preparation of CmF_3 by the action of an excess of NH_4HF_2 on CmO_2 [154] have been described; in all cases, the reactions began at 110–125°. The fluorination of uranium dioxide has been studied in most detail. As early as 1943, it was shown that the reaction takes place at 150–200°;[312] higher temperatures are required to increase the degree of fluorination.[312–314] The reaction of UO_2 with NH_4HF_2 is exothermic[315] and takes place at 150–170° to give $(NH_4)_2.UF_6$.[136,316] The product of the reaction of UO_3 with concentrated NH_4HF_2 solutions is $(NH_4)_3UO_2F_5$.[142,143] UO_3 can also be fluorinated in the absence of a solvent.

The reaction of TiO_2 with NH_4HF_2 begins at a temperature of ~100° [158] to give $(NH_4)_2TiF_6.NH_4F$.

Zirconium dioxide reacts with NH_4HF_2 to give $(NH_4)_3ZrF_7$ [317] or $(NH_4)_2ZrF_6$.[160,318,319] The reaction is most vigorous after the NH_4HF_2 melts.[282,320,321] Treatment with ammonium hydrogen fluoride reduces the concentration of oxygen in ZrF_4 to 0.25%.[322]

NH_4F solution at temperatures of 450–700° and pressures of 800–3000 atm can be used to grow single crystals of TiO_2, ZrO_2, and HfO_2.[323]

The reaction of V_2O_3 with NH_4HF_2 in the ratio 1 : 8 or 1 : 2 at 185–200° for 2 h gives the green compound $(NH_4)_3VF_6$.[182] A mixture of V_2O_5 and NH_4HF_2 reacts at 95° to give $(NH_4)_3VO_2F_4$.[178]

Stoichiometric mixtures of Ta_2O_5 or TaO_2F with NH_4HF_2, with gentle heating, give $(NH_4)_2TaF_7$.[184] Under analogous conditions, the niobium compounds form $(NH_4)_3NbOF_6$.

According to Ref.324, the reaction of CrO_3 with NH_4F in aqueous solution gives $(NH_4)_2Cr_2O_7$ and HF.

The reaction of MoO_3 with NH_4HF_2 at a molar reagent ratio of 1 : 2 and a temperature of 105–110° leads to the exothermic formation of $(NH_4)_2MoO_2F_4$.[196,199] At lower temperatures, $(NH_4)_3MoO_2F_4$ is formed.[196] A stoichiometric mixture of WO_3 and NH_4HF_2 at 190–200° is converted into $(NH_4)_3WO_2F_5$.[197] The reactions of molybdenum and tungsten trioxides with aqueous NH_4F solutions give the salts $MO_3.nNH_4F$.[200,205]

The reaction of ReO_3 with NH_4HF_2 has been studied only qualitatively; its products are volatile oxide fluorides.[325]

The reaction of Fe_2O_3 with NH_4HF_2 takes place at 170° to give $(NH_4)_3FeF_6$.[69] NH_4HF_2 apparently reacts readily with other iron oxides, since ammonium fluorides have been recommended for the simultaneous removal of rust and sand from the surface of iron tubes.[326]

The higher oxides of other transition metals (manganese, cobalt, nickel, etc.) also apparently react with ammonium fluorides. Alumina heated at high temperatures is apparently the oxide most resistant to the action of ammonium fluorides. Oxides can be fluorinated using fluorometallates. This process has been described for Al_2O_3 [71,327] and BeO.[328]

The above data confirm the conclusions reached in Ref.329: NH_4HF_2 begins to react with oxides at 70–130°, the reactions are most vigorous after the NH_4HF_2 melts, and the reactivity of NH_4HF_2 (to give fluorometallates) is often greater than that of anhydrous hydrogen fluoride.

4. Reactions with Salts

A large number of reactions of ammonium fluorides with salts have been reported. For example, the conversion of calcium chloride into the fluoride by boiling an aqueous solution containing NH_4F,[330,331] of MgCl solution into $(NH_4)_2.MgF_4$,[58] of cadmium salt solutions into CdF_2,[20] and of solutions of lanthanide chlorides into the trifluorides[332] have been described. Phosphorus chlorides and oxide chlorides, and arsenic and silicon chlorides, although not salts, are fluorinated when boiled under reflux with NH_4F.[333]

The ammonium fluorometallates of many metals can be obtained by the reactions of the bromides or nitrates with NH_4F in methanol.[99,334,335] The conversion of $Th(NO_3)_4$ solution into ammonium fluorometallates[125] and the conversion of $NaNO_3$ into $NaHF_2$ [260] have been described.

Carbonates are often used as the starting materials for preparing fluorides. The carbonates and ammonium fluorides have been used to prepare lithium fluoride,[336] cerium trifluoride,[387] fluorides for luminophors,[338] and $(NH_4)_2MgF_4$,[58] and the hydroxide carbonates have been used to prepare fluoro-complexes of cobalt and nickel.[219] Treatment with anhydrous NH_4F or its solutions can be used to remove traces of $CaCO_3$ from CaF_2.[294,298] (The mechanism and kinetics of this process have been described.[338–341]) NH_4HF_2 can be used to obtain lanthanide fluorides from concentrates containing carbonates,[342] and also KHF_2 from K_2CO_3.[343]

Ammonium fluorides have also been used to fluorinate sulphates,[344–347] silicates,[9,348] phosphates,[349,350] magnesium acetate,[351] beryllium oxide acetate,[352] sodium aluminate,[346] ammonium vanadate,[178] ammonium tungstate,[197] calcium tungstate,[13–15] ammonium molybdate,[197] lithium hydroborate,[353] cerium(III) oxalate,[337] and various minerals and concentrates with complex compositions.[10–12,354]

The salts of most acids probably react with ammonium fluorides to give the corresponding fluorides. The formation of double salts is a somewhat unique phenomenon; they are few in number, however, and are known only for ammonium nitrate and perchlorate.[60,355–358]

V. CONCLUSION

In the research literature, including recent publications, it is still possible to find ammonium fluoride regarded as a complete analogue of other ammonium halides. Because of the formation of strong additional hydrogen bonds, however, many of the properties of ammonium fluoride differ sharply from those of compounds of NH_3–HX systems, where X = Cl, Br, or I. The most characteristic difference shown by the fluorides is the ability of the NH_3–HF system to form stable hydrogen salts: ammonium hydrogen fluoride even has a higher thermal stability than ammonium fluoride.

Ammonium fluorides also differ considerably from other ammonium halides in their reactivity, due to the specific properties of inorganic fluorides, namely the high strength of element–fluorine bonds (high enthalpy of bond rupture), and the consequent high values of the enthalpies and Gibbs free energies for many fluorination reactions.

In the series of traditional fluorinating agents (fluorine, halogen fluorides, anhydrous hydrogen fluoride, and hydrofluoric acid), ammonium fluorides, in particular ammonium hydrogen fluoride, occupy an intermediate position between fluorine and anhydrous hydrogen fluoride, often giving higher values than the latter for the equilibrium constants and rates of fluorination.

As shown above, ammonium fluorides can be used to fluorinate various elements, many oxides, and a very large number of salts (metallates).

The fluorination of the oxides of the non-transition elements of groups II–IV gives the higher fluorides or the corresponding fluorometallates, whereas the fluorination of the oxides of the non-transition elements of group V gives the oxide fluorides or oxofluorometallates. For the higher oxides of the transition metals, the "boundary" between the tendency to form completely fluorinated products (fluorides and fluorometallates) and the tendency to give oxide fluorides or oxofluorometallates corresponds to the centre of the periodic system; the oxides of the group IV metals form fluorometallates, and the oxides of the group VI metals form oxofluorometallates. An interesting feature is that V_2O_5, Nb_2O_5, and Ta_2O_5 under identical conditions react with NH_4HF_2 to give compounds of different types: $VO_2F.nNH_4F$, $NbOF_3.nNH_4F$, and $TaF_5.nNH_4F$. A decrease in the oxidation state of the metal in the oxide brings it closer to the elements of groups with a smaller number. Thus on fluorination, V_2O_3 behaves like a group III element and gives derivatives of VF_3; UO_3 is converted into $(NH_4)_3UO_2F_5$, resembling to some extent MoO_3 and WO_3, whereas the behaviour of UO_2 (which is converted into UF_4 derivatives) is closer to that of ZrO_2.

The thermal decomposition of fluoro-derivatives of Ce^{IV}, Mn^{III}, Pu^{IV}, and Cm^{IV}, and also oxofluoro-derivatives of V^{V}, Mo^{VI}, and W^{VI}, involves partial reduction in the last stages. This phenomenon should also be characteristic of salts of Cr^{IV}, Re^{VIII}, Re^{VI}, and other metals of group VII, and also of all the actinides following plutonium.

In an excess of NH_3, reduction may be accompanied by the ammonolysis of the simple fluorides. The question of the possibility of ammonolysis during thermal decomposition remains open. Heating simple fluorides in an ammonia atmosphere up to 300–900° gives nitrides or nitride fluorides.[359–364] A mixture of molybdenum nitride and trifluoride was detected in the thermal decomposition products of ammonium fluoromolybdate,[203] although these data require confirmation.

The behaviour of nitrogen in the last stages of the thermal decomposition has been little studied. The removal of small quantities even as ammonia is kinetically hindered (this is characteric, for example, of vanadium(III) [182]) because of mechanical blocking, the formation in a number of cases of solid solutions of the fluorometallates in the fluorides, or, as in the case of the lower oxide fluorides of tungsten and molybdenum, because of the introduction of ammonium ions into the cavities of the crystal lattice. These effects possibly also lead to erroneous conclusions about the formation of "new phases", with lower ammonium fluoride concentrations (see for example Refs.7 and 135). An increased concentration of residual nitrogen lowers the quality of the fluorides obtained, and is particularly undesirable when fluorides are used to prepare metals.

An interesting and little studied problem concerns the preparation of volatile fluorides using ammonium fluorides. The action of heat on many ammonium fluorometallates leads to the transfer of the metal fluorides (for example titanium, niobium, tantalum) to the gas phase, and the problem reduces to the separation of mixtures of these fluorides, ammonia, and hydrogen fluorides, which on simple cooling react again to re-form fluorometallates with the same or different compositions. The selective trapping of TiF_4 on CaF_2 at 300–350° has been proposed[365] for the separation of TiF_4 from its mixtures with NH_3 and HF.

The available published thermodynamic data on ammonium fluoro- and oxofluorometallates are unfortunately as yet insufficient for making any generalisations, predictions, or estimations.

Although various reactions of ammonium fluorides and properties of ammonium fluorometallates still require further study, it may be concluded that a fairly wide range of inorganic fluorides can be synthesised using ammonium fluorides.

The most urgent problems in further research in this direction are related primarily to the measurement of the enthalpies of formation, decomposition pressures, and heat capacities of fluoro- and oxofluorometallates, the study of the mechanism and kinetics of all the stages (particularly the last stages) of the thermal decomposition of fluoro- and oxofluorometallates, and the study of the reactions of ammonium fluorides with oxides, metallates, and minerals.

While the present manuscript was being prepared for publication, a number of publications related to its various sections appeared. Thus an indirect method has been used[366] to measure the degree of decomposition of NH_4F in the gas phase, and it has been shown that at 288.9 K, when the total vapour pressure is 0.40 Pa, the degree of decomposition is only 0.97. Strange as it may seem, even lower values were obtained for other ammonium halides. At the same time, a new measurement of the enthalpy of decomposition of NH_4HF_2[367] gave a result (about 51.5 kcal $mole^{-1}$) differing little from the value previously adopted.

The study of the fusion diagram of the NH_4F–HF system has been repeated, a number of new ammonium hydrogen fluorides have been detected, and the crystal structures of $NH_4H_3F_4$, $NH_4H_4F_5$, and $NH_4H_7F_8$ have been studied.[368] The enthalpies of solution of NH_4F and NH_4HF_2 in water have been measured again.[369]

Published calorimetric data on the enthalpies of formation of NH_4ZnF_3 and NH_4CdF_3 (−295.3 kcal $mole^{-1}$ and −286.8 kcal $mole^{-1}$) [370,371] make it possible to eliminate the contradiction noted in the text of the present review, and indicate that the results obtained in Ref.100 are too low. The enthalpies of the separate stages of the thermal decomposition of $(NH_4)_3WO_2F_5$ and the overall enthalpy of decomposition to W_2O_4F (109 kcal $mole^{-1}$) have been determined.[372]

Hydrothermal synthesis in NH_4HF_2 has been used to synthesise $NH_4Fe^{2+}Fe^{3+}F_6$, NH_4MnFeF_6, and NH_4MnCrF_6,[373–375] which are isostructural with one another and have a previously unknown structure. The thermal properties of these unusual fluorometallates have been studied.

New data on the reactions of ammonium fluorides have been published. Thus the reaction of an equimolar mixture of CrO_3 and NH_4HF_2 in the presence of small quantities of water has been used to synthesise NH_4CrO_3F;[376] the thermal decomposition of this compound is accompanied by the reduction of Cr^{6+} to Cr^{3+}.

The reaction of nickel and cobalt oxide carbonates and hydrated fluorides with ammonium fluorides has been studied in more detail.[377] The reactions of NH_4F with XeF_2, XeF_6, and KrF_2 [378] give N_2, HF, and Xe (or Kr). In the presence of metals (Fe, Cr), the compounds NH_4MF_4 are also formed.

According to Ref.379, the reaction of NH_4HF_2 with $NaVO_3$ and NH_4VO_3 gives $(NH_4)_2NaVO_2F_4.H_2O$ and $(NH_4)_3VO_2F_4.0.5H_2O$. The published[379] thermal decomposition schemes assume that the compounds give up NH_4F in three stages, but retain water of crystallisation. This does not agree with the general regular features of processes of this kind (ammonium fluorometallates have a higher thermal stability than the metal fluoride crystalline hydrates), X-ray diffraction data (the presence of water of crystallisation would change the structures of the compounds), and the results of earlier studies.[178,180] The process proposed in Ref.178, however, also requires refinement, with allowance for the observed[379] reversible phase transformation of $(NH_4)_3VO_2F_5$ (408 K; ~0.6 kcal $mole^{-1}$).

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Mendeleev Moscow Institute
of Chemical Technology
Institute of Chemistry,
Far Eastern Research Centre,
Academy of Sciences of the USSR,
Vladivostok

Translated from *Uspekhi Khimii*, 53, 1493-1522 (1984) U.D.C. 543.515/547.21 + 547.5 + 547.6

Mass Spectrometry of Saturated Hydrocarbons

L.S.Golovkina, G.V.Rusinova, and Al.A.Petrov

The decomposition by electron impact of saturated acyclic and cyclic (mono-, bi-, tri-, tetra-, penta-, and hexa-cyclic) hydrocarbons having condensed, bridged, and single-bonded structures is examined and the reaction mechanisms, the characteristics of the decomposition due to structural and stereochemical factors, and the possibilities for the identification of the hydrocarbons by analysing their mass spectra are discussed.
The bibliography includes 204 references.

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I. INTRODUCTION

The basis on which mass spectrometry has been established as an analytical method has been its successful application in qualitative and quantitative analyses of hydrocarbon mixtures, in particular, petroleum and its processing products as well as the products of the petrochemical and organic synthesis. The subsequent stage in the development of this method was determined by the combined employment of highly effective procedures for the separation of mixtures and the automation of the interpretation of the mass spectrum which led to the development of fundamentally new mass-spectrometric analytical methods.

Chromato-mass-spectrometry has become irreplaceable in the analysis of hydrocarbons and their mixtures by virtue of the large amount of information derivable by this procedure, its sensitivity, and the speed and accuracy of the determinations. The advances in this field are based on the systematic study of the characteristics of the mass-spectrometric decomposition of individual hydrocarbons. In contrast to compounds with functional groups, where the heteroatom is generally the site of the preferential localisation of charge and hence determines which particular bond is ruptured preferentially, for a hydrocarbon molecule it is difficult to isolate such a decisive factor, i.e. it is difficult to interpolate the mass spectrum even within the limits of a narrow group of compounds. The low predictive power of the mass spectra of hydrocarbons (with the exception of n-alkanes), where the appearance of even one non-bonding interaction can lead to significant changes in the spectrum, the large number of isomeric and stereoisomeric structures, the monotonic variation of their mass spectra, and the associated difficulty of the computer search in their identification necessitate a detailed investigation and periodic systematic treatment of the mass spectra of hydrocarbons as well as the analysis and survey of the information in this field, which is constantly being renewed and expanded.

The review below is devoted to the characteristic features of the decomposition of saturated hydrocarbons under electron impact.

II. ALKANES

Alkanes constitute a large proportion of petroleum and their mass spectra have been described in the greatest detail.[1-7] The spectra of unbranched normal alkanes are very similar. The curve for the distribution of the peak intensities in their spectra (Fig.1) decreases smoothly from a maximum in the region of mass numbers of 43, 57, and 71 to the peak of the molecular ion (MI). The appearance of a maximum at any position on this curve implies the presence of a branch in the alkane molecule (Fig.2). The above features of the mass spectra of normal alkanes and alkanes substituted at different sites (including isoprenoid alkanes) are used for analytical purposes[8-13] although the information obtained from the consideration of the mass spectrum is insufficiently specific for the complete identification of any alkane.

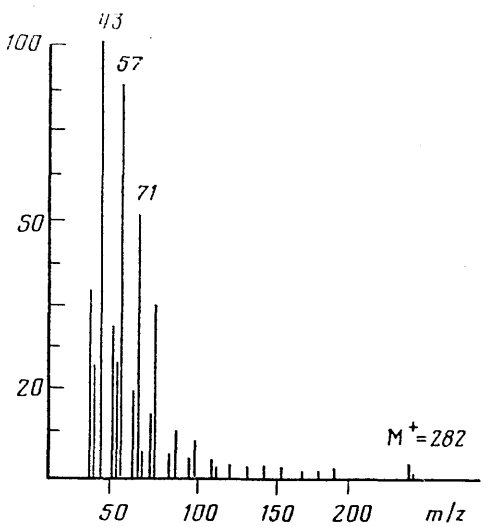


Figure 1. The mass spectrum of n-eicosane.[41]

The intensity of the MI peaks of n-alkanes is low and decreases exponentially with increased molecular weight of the alkane.[14] The intensities of the MI peaks of branched alkanes depend on the number and relative positions of the methyl groups and decrease with increase in the degree of branching.[1,8,14]

A whole series of communications (among them also reviews),[9,15-29] including the analysis of the mass spectra of n-alkanes labelled with ^2H [15,17-19] and ^{13}C,[20-23] thermochemical data for the molecular and fragment ions,[24,25] low-temperature spectra,[29] ionisation efficiency curves,[5] reactions occurring on collision with a gas molecule,[16,23] etc. have been devoted to the structure and mechanism of the decomposition of molecular and fragment ions derived from n-alkanes. This analysis permitted the conclusion that the reactive configuration of the MI retains to a large extent the structure of the neutral molecule, while fragment ions decompose via complex skeletal rearrangements, which accounts for the observed loss of identity of the peaks of labelled ions in a series of mass spectra of lower n-alkanes.[15]

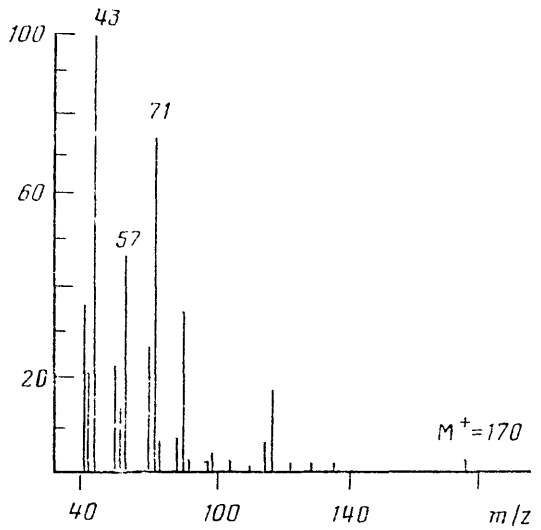
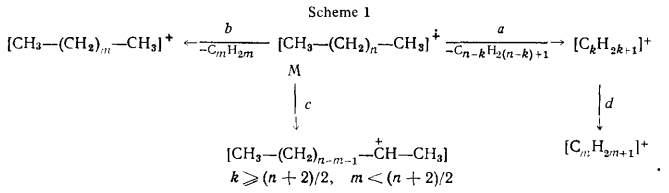


Figure 2. The mass spectrum of 4,7-dimethyldecane.[2]

The alkyl ions C_kH_{2k+1} are formed with the highest probability by simple rupture of the C–C bonds in the MI (Scheme 1, pathway *a*). This process is most favoured in the formation of large ions [$k \geq (n+2)/2$].[9,15,20]

Scheme 1



The study of the mass spectra of a large series of n-alkanes showed that there is a relation between the intensity of the peak of the alkyl ion C_kH_{2k+1} and the number of carbon atoms in the molecule (n) and fragment (k) ions.[9,15] The study of metastable transitions and ionisation efficiency curves[5] and comparison of the low-temperature mass spectra obtained for high (70 eV) and low ionisation energies[29] have shown that small alkyl ions are formed mainly via secondary processes, i.e. as a result of the decomposition of heavier primary alkyl ions (Scheme 1, pathway *d*). The few ions which are formed directly from the MI are produced from its central component (Scheme 1, pathways *b* and *c*) in the non-specific dissociation of the C–C bonds with recombination of the terminal methyl groups.[15,20] The contribution of this pathway increases with increasing chain length.

The probability of the loss of the methyl group is low and diminishes with increase in the n-alkane chain length.[22] The elimination of the CH_3 group proceeds to a large extent non-specifically: the formation of $[M-CH_3]^+$ is associated with the elimination of both terminal carbon atoms (pathway *a*) and the carbon atoms in the central component of the molecule (pathway *c*).[22] The formation of ions with an odd number of electrons is associated with the rearrangement of H atoms[28] or CH_3 groups.[18]

III. MONOCYCLIC SATURATED HYDROCARBONS

1. Unsubstituted Monocyclic Hydrocarbons

The mass spectra of unsubstituted monocyclic hydrocarbons having the general formula  are known for compounds with n = 3–14 and 24.[2,30-41] The character of the variation of the MI peak intensities in the series of C_3–C_{14} cycloalkanes is described by a curve[30] having maxima in the region of n = 3, 6, and 13 and a distinct minimum in the region of n = 9 and 10. The molecular ion of cyclopropane is the most stable in the series of cycloalkanes and its intensity is a maximum in the spectrum. A distinctive feature of this spectrum is the presence of a peak due to the ion $[M-3H]^+$,[2,32] whose high intensity can be explained by the aromatic character of the cyclopropenyl cation $[C_3H_3]^+$ formed.[33]

The study of the mechanisms of the fragmentation of cycloalkanes with the aid of deuterated analogues,[34,35] the measurement of the ionisation potentials and the heats of formation of their molecular ions,[36,37] and the study of the kinetics of the isomerisation of the MI [38,39] showed that, under the conditions of electron impact, the MI of cycloalkanes with three–five-membered rings undergo intensive isomerisation to linear ions, while the MI of hydrocarbons with six–eight-membered rings mainly retain the cyclic structure.

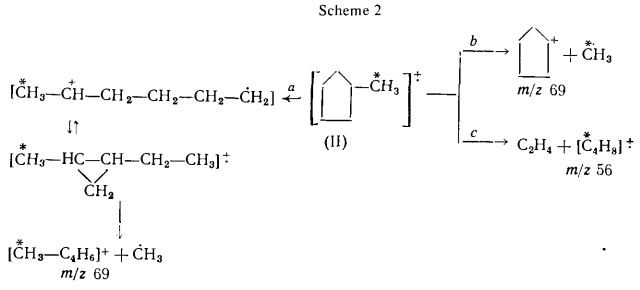
Despite the different structures of the MI of hydrocarbons with different ring sizes, the mass spectra of compounds with four–eight-membered rings are in many respects similar. They are characterised by the intense peak of the ion $[M-CH_3]^+$ and the peak for one of the odd-electron ions (m/z 56, 70, etc.) is the most intense in their spectra.[2,30,40] An increase of ring size alters appreciably the pattern in the decomposition of the MI and the character of the spectrum of the hydrocarbon containing more than eight carbon atoms in the molecule becomes similar to that of the spectrum of the corresponding alkane: the stability of the MI is low and the peaks of the even-electron ions (m/z 57, 71, etc.) predominate in the spectrum.[2,30,31] The high intensity of the MI peak in the spectrum of cyclotetracosane should be noted as an exception.[41]

2. Monosubstituted Monocyclic Hydrocarbons

The introduction of the methyl substituent into the cycloalkane molecule does not eliminate the differences noted between the structures of the molecular ions of unsubstituted

hydrocarbons. It has been suggested[40,42–44] that the ionisation of the MI of methylcyclopropane (I) and methylcyclopentane (II) entails the rupture of the endocyclic bond adjoining the methyl group and that, after the migration of the proton, an alkene ion with a straight-chain structure is formed [the n-butene ion for (I) and the n-hexane ion for (II)]. For methylcyclopropane, this conclusion has been confirmed by the identity of the spectra of compound (I) and its acyclic isomers.[42] Analysis of the spectra of methylcyclopentane and methylcyclohexane (III) analogues deuterated in all positions and labelled with ^{13}C permitted a detailed study of all the possible pathways leading to the formation of the fragment ions (Scheme 2; the ^{13}C isotope is marked with an asterisk) and also an estimate of the contribution of each pathway to the overall peak intensity of the ion having the given mass.[43–46]

Scheme 2

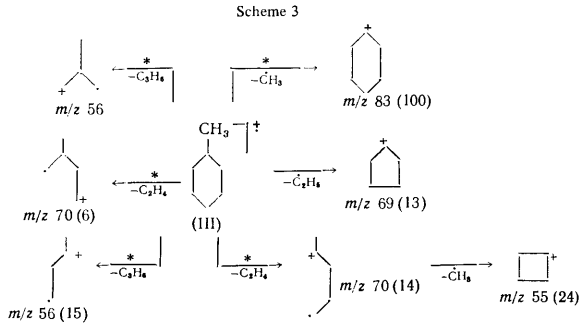


The data obtained for compound (II) show that the molecular ion decomposes with a higher probability via pathway *a*.[43–44]

Another intense process involving the decomposition of the molecule of compound (II) is the elimination of ethylene from the MI. The study of the mass spectra of the deuterated analogue of compound (II) showed[45] that the C_2H_4 molecule is ejected mainly from the cyclic component of the MI (Scheme 2, pathway *c*).

In methylcyclohexane, whose MI retains mainly the cyclic structure, the elimination of the methyl group takes place only from the side chain.[45] Scheme 3† presented below, constitutes the generalised result of a study which showed[46] that more than 90% of the primary fragment ions are formed on dissociation of the C–C bond at the tertiary carbon atom of the MI (the relative peak intensities expressed as percentages are indicated in brackets):

Scheme 3



The ratios $I_{[M]^+}/I_{[M-CH_3]^+} < 1$ have been obtained for methylcycloheptane and methylcyclo-octane, as for compound (II) and (III). On further increase of ring size, the $[M-CH_3]^+$ peak diminishes and is not observed at all in the spectra of methylcyclodecane, methylcyclododecane, and methylcyclotetracosane.[2,41]

The existence of the isomeric linear form of the MI has also been noted for ethyl and propyl derivatives of cyclopropane and cyclopentane,[45–47] although it has been shown for ethylcyclopentane[45] that the weakening of the bond between the ring and the substituent results in an equal probability of the two processes involving the abstraction of the substituent from the MI (pathways *a* and *b* in Scheme 2). The intensity of the MI peak in the spectra of monoalkylcyclopentanes [Alk = n-Pr, n-Bu, t-Bu, n-C_3H_{11}, iso-C_5H_{11}, n-$C_{16}H_{33}$, or $CH(C_9H_{19})_2$] and cyclohexanes (Alk = C_2H_5–$C_{10}H_{21}$, iso-Pr, s-Bu, iso-Bu, or t-Bu)[48] varies appreciably as a function of the length and structure of the substituting group.[48,49] The most intense peak in the spectra of monoalkylmonocyclanes is that of the ion $[M-R]^+$. The intense peak of the ion $[M-RH]^+$ accompanies it. This pair of peaks (*m/z* 83, 82 for alkylcyclohexanes and *m/z* 69, 68 for alkylcyclopentanes) is used for the qualitative and quantitative analyses of these two types of hydrocarbons in mixtures.[50–55] There are also literature data on the mass spectra of alkylcyclohexanes and alkylcyclopentanes obtained using different energies of ionising electrons.[50,51,56]

3. Polysubstituted Monocyclic Hydrocarbons

Among polysubstituted monocyclanes, alkylcyclopentanes (ACP) and alkylcyclohexanes (ACH) have been studied in greatest detail. Analysis of the mass spectra of the structural and geometrical isomers revealed the influence of ring size and the number, nature, and relative disposition of the substituents in the molecule on the mechanism of the decomposition of the MI.[57–68]

An increase of the number of methyl groups in the methylcycloalkane molecule as a rule decreases the peak for the ion $[M-CH_3]^+$ and increases the intensity of the peaks due to the ions formed on decomposition of the ring, but has little influence on the stability of the MI[68] (Table 1). The appearance in the molecule of a more stable group R entails a decrease of the intensity of the MI peak and an increase of the intensity of the peak due to the ion $[M-R]^+$.

Table 1. The peak intensities of the ions M^+ and $[M-R]^+$ in the mass spectra of alkylcyclopentanes (ACP) and alkylcyclohexanes (ACH).[68]

N	$I_{[M]^+}$		$I_{[M-CH_3]^+}$		$I_{[M-C_2H_5]^+}$	
	ACP	ACH	ACP	ACH	ACP	ACH
1	3.0–0	9.2–0.3	9.5	22.5	16.2	27.3
2	3.7–0.6	6.3–0.3	4.7–2.5	26.8–13.1	18.2–13.0	31.7–26.6
3	3.1–1.2	6.4–1.1	2.6–0.9	24.0–3.5	11.8–2.4	24.5–14.0
4	2.3–0.1	5.4–3.4	0.7–0.2	16.8–0.7	8.3–1.3	–
5	3.2–0.6	4.9–2.4	1.5–0.2	9.2–0.5	—	–
6	—	5.8–2.1	—	8.5–0	–	–
gem	2.4–0.1	2.8–0	15.0–3.0	31.6–5.5	—	30.9–18.0

Remarks: R = CH_3 for the methyl-substituted derivatives and R = C_2H_5 for the ethyl and methylethyl-substituted derivatives; *N* is the number of substituents in the molecule. Here and henceforth the peak intensities are quoted as percentages of the total ion current.

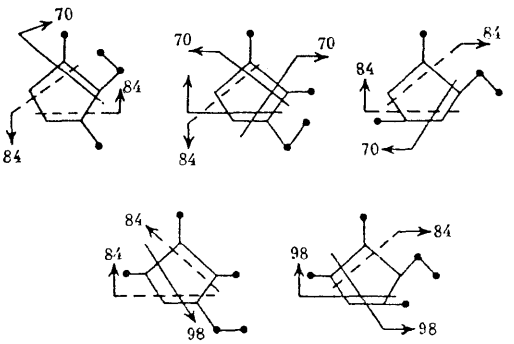
The molecular ions of hydrocarbons of the cyclopentane series, whose molecules contain a ring more strained than in cyclohexanes, decompose via two competing pathways with

†In Scheme 3 and henceforth the asterisk denotes the presence of a peak due to a metastable ion (MSP).

equal probabilities: (1) abstraction of the alkyl substituent R from the molecular ion with subsequent decomposition of the ion $[M-R]^+$ formed; (2) decomposition of the cyclic component of the molecule. The decomposition of the cyclic component leads mainly to the formation of ions with an odd number of electrons (Scheme 2, pathway *c*).

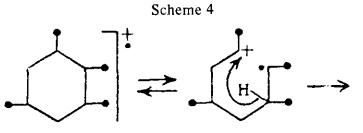
The mass spectra of the structural isomers of dialkylcyclopentanes differ only in the intensities of the peaks due to ionic species M^+ and $[M-RH]^{+\cdot}$, the first peak being more intense in the spectra of 1,2-substituted derivatives and the second in those of the 1,3-substituted derivatives.[49,65]

The differences between the spectra of the structural isomers of tri- [57] and tetra-alkylcyclopentanes[58] are expressed mainly in the different intensities of the peaks for ions with *m/z* 70, 84, 98 formed on decomposition of the cyclic component of the molecule.

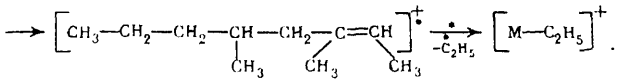


In contrast to alkylcyclopentanes, the decomposition of the cyclic components of the molecules of alkylcyclohexanes occurs only for structures having a vicinal disposition of the methyl groups in the molecule. It involves the formation of both odd-electron ions, for example, $[M-C_2H_4]^{+\cdot}$ and $[M-C_3H_6]^{+\cdot}$, and even-electron ions, for example, $[M-C_2H_5]^+$. The appearance of the latter can be explained by the decomposition of the isomeric linear form of the MI whose formation is initiated by the presence of vicinal substituents.[60,67,68] This also accounts for the appearance of the peak due to the ion $[M-C_2H_5]^+$ in the spectra of hydrocarbons with the MI (IV), which lack an unsubstituted dimethylene unit whose elimination together with the proton might also lead to the formation of the ion $[M-C_2H_5]^+$ (Scheme 4).[60]

Scheme 4



M, (IV)



Additional evidence for the existence of the isomeric form of the MI is provided by the absence of correlation between the stability of the MI and the relative stabilities# in the series of geometrical isomers as well as the presence of such correlation for the primary ions formed in the competing decomposition reactions of the isomeric forms of the MI.[60]

#Here and henceforth thermochemical stability (ΔH) is referred to.

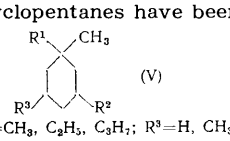
In the series of structural isomers of di-, tri-, and tetramethylcyclohexanes the peak intensities of the ionic species formed on decomposition of the cyclic component of the molecule, namely $[M-C_2H_5]^+$ and $[M-C_3H_6]^{+\cdot}$, increase and the intensity of the ion $[M-CH_3]^+$ formed in a competing process falls as the stability of the isomer diminishes.[60] For the 1,3- and 1,4-dimethyl- and 1,3,5-trimethyl-cyclohexanes, which have no vicinal methyl groups in the molecule, the MI decomposes only via the first pathway. They are characterised by the maximum intensity of the peak due to the ion $[M-CH_3]^+$ in the series of structural isomers.

The quantitative differences between the spectra of the structural isomers of di-, tri-, tetra-methylcyclohexanes, reflecting the contribution of a particular pathway in the decomposition of the MI, make it possible to identify each isomer, with the exception of 1,3-, and 1,4-dimethylcyclohexanes, on the basis of the criteria presented (Table 2).[68]

Table 2. Diagnostic features of the mass spectra of structural isomers of di-, tri-, and tetra-methylcyclohexanes.

Di-	I_{70}/I_{83}	Tri-	I_{84}/I_{83}	I_{97}	Tetra-	I_{84}/I_{97}	I_{98}/I_{97}
1,2-	$\geqslant 1$	1,2,3-	$\leqslant 1$	8,6—2,2	1,2,4,5-	>1	>1
1,3-	$\leqslant 1$	1,2,4-	>1	5,0—1,2	1,2,3,5-	$=1$	$\leqslant 1$
1,4-	$\leqslant 1$	1,3,5-	$\leqslant 1$	0,7—0,5	1,2,3,4-	<1	$\geqslant 1$

For cyclohexanes having a substituent R other than the methyl group, the decomposition of the MI take place mainly in accordance with the first pathway. The differences between the spectra of these structures are associated solely with the intensity of the peaks for the ionic species M^+, $[M-R]^+$, and $[M-RH]^{+\cdot}$ and as a rule have no diagnostic value.[60] However, the position of the group R in the molecules of geminal-substituted cyclohexanes (V) can be readily determined mass-spectrometrically.[2,68] The spectra of geminally substituted cyclopentanes have been little studied.[2]



(V)

R^1, R^2=CH_3, C_2H_5, C_3H_7; R^3=H, CH_3

Systematic study of the mass spectra of monocyclic hydrocarbons has shown no possibility for an unambiguous assignment of the hydrocarbon to the cyclopentane or cyclohexane series solely on the basis of one characteristic feature. However, when the molecule contains at least one methyl substituent, this can be achieved on the basis of a number of features which are proposed in Table 3. The same data permitted conclusions concerning the number *N* of substituents in the ring.

The presence of two and more substituents in the ring implies the possibility of the existence of stereoisomers. Under these conditions, in the case of compounds without heteroatoms, the influence of the steric structure on the decomposition of the molecule can be very considerable and in a number of instances[68] can swamp the effect of structural isomerism. This influence is natural if one takes into account the absence of a site of preferential localisation of the charge in the saturated hydrocarbon molecule—a factor which is as a rule of decisive importance in the decomposition of heteroatomic compounds. Thus only the energy state of the molecules of isomeric hydrocarbons, determined by the

number of non-bonding interactions, determines the mass-spectrometric properties.

The idea of a relation between the relative stabilities of the stereoisomers and the differences between their spectra was put forward by Biemann[69] as early as 1962 and was then developed in a whole series of studies by Natalis and co-workers.[70-74] Subsequently Meyerson[75] related these differences to the thermochemical stabilities, i.e. the enthalpies of the ground states of the ions, which determine the ease of the fragmentation reactions, and not to the thermodynamic stability of the isomer—a factor which is significant for the relative proportions of the isomers under equilibrium conditions. This conclusion is consistent with the ionisation energies (IE) and appearance energies (AE).[71,76]

Table 3. Diagnostic features in the mass spectra of hydrocarbons of the cyclopentane and cyclohexane series and the values of m/z for the peak with maximum intensity.

	Cyclopentanes		Cyclohexanes	
N	(m/z)	diagnostic features	(m/z)	diagnostic features
		C_9H_{18} (M=126)		
1	69	intense peaks of ions with m/z 68, 69	83	intense peaks of ions with m/z 82, 83
2	83, 55	intense peaks of ions with m/z 83, 55; $I_{97}<2$	97, 55	intense peaks of ions with m/z 97, 55
3	55, 56, 70	I_{97}=2.4—11.8	69	intense peaks of ions with m/z 69, 111*
4	84, 69, 70, 98	$I_{97}\leqslant 1.5$; $I_{111}<1$	—	—
		$C_{10}H_{20}$ (M=140)		
1	69	intense peaks of ions with m/z 68, 69	83	intense peaks of ions with m/z 82, 83
2	—	—	97, 55	intense peaks of ions with m/z 97, 55; absence of peaks of ions with m/z 70,84
3	97, 55	I_{84}=3.5—3.8; I_{70}=8.7—9.6	69	intense peaks of ions with m/z 69, 111; $I_{97}>I_{98}$; $I_{125}<1$**
4	69, 98	$I_{98}\gg I_{97}$; $I_{125}<1$	69	I_{125}=2.0—12.2
5	84	—	—	—

*The spectrum of 1,2,3-trimethylcyclohexane is an exception, but for this spectrum $I_{83}>I_{84}$, in contrast to the spectra of trialkylcyclopentanes.

**The spectrum of 4-ethyl-1,2-dimethylcyclohexane is an exception. It resembles the spectra of the series of stereoisomers of tetramethylcyclohexane.

Measurements performed with the aid of photoionisation for a series of 1,2-dimethylcyclopentanes and cyclohexanes have shown[71] that the IE of the stereoisomers do not differ, while the AE of the ions $[M-CH_3]^+$ {for dimethylcyclopentanes, also the ions $[M-C_2H_4]^+$, $[M-C_2H_5]^+$, $[M-C_3H_5]^+$, and $[M-C_3H_6]^+$} change by 0.1 eV on passing from the *cis*- to the *trans*-isomer. Within the limits of experimental error, this difference is in each case equal in magnitude (but opposite in sign) to the difference between the heats of formation of the stereoisomer. Somewhat different values but showing the same type of variation as a function of the relative positions of the substituents have been obtained for the stereoisomers of 1,2-dimethylcyclohexane by other methods.[77,78]

The interrelation of the stereochemistry of the molecule and of the characteristic features of its decomposition under electron impact has been traced in detail and systematically for almost all the stereoisomers in the series of polymethylcyclopentanes and polymethylcyclohexanes.[2-5,49,57-68] The character of the variation of the quantitative characteristics of the spectrum remains the same as in the series of structural isomers: the intensity of the peaks due to the ions $[M-R]^+$ is a maximum in the spectrum of the isomer showing the highest thermochemical stability and decreases with decrease of the stability in the series of stereoisomers; there is a simultaneous increase of the intensities of the peaks due to the ions formed on decomposition of the cyclic component of the molecule.

The differences between the quantitative characteristics of the spectra of the stereoisomers are greater the larger the difference between the stabilities of their molecules. In a number of instances these differences are of diagnostic value.[57-60] The spectra of stereoisomers whose stabilities are similar are virtually identical.

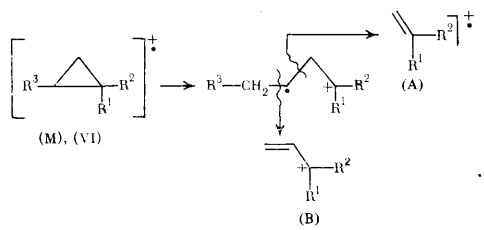
The available information about the decomposition of substituted cycloalkanes C_nH_{2n} (where $n\neq 5$ or 6) under electron impact is limited to data concerning alkylcyclopropanes. In the spectra of geminally (R^1=R^2=CH_3, R^3=H) and vicinally (R^1=R^3=CH_3, R^2=H) substituted dimethylcyclopropanes (VI)[132] the peak for the ion $[M-CH_3]^+$ shows the highest intensity. The absence of appreciable differences between their spectra has been attributed to[32] the pseudo-ethylenic character of the bonds in the cyclopropane ring. This hypothesis is supported by the large number of peaks due to doubly charged ions.[69]

The mass spectra of isomeric cyclopropanes differing in the lengths of the alkyl substituents R^1 and R^2 (i.e. in the position of the cyclopropane ring in the aliphatic chain) also proved to be similar.[79] The absence of differences between the spectra of dialkylcyclopropanes (VI) and the corresponding olefins (there are differences only in the stabilities of the MI) demonstrates the possibility of the isomerisation of the MI compound (VI) to an ion having a linear structure.

A distinctive feature of the spectra of the hydrocarbons (VI) is the presence of intense peaks of the ions formed on dissociation of the C—C bonds in the ring at one of the carbon atoms [ions of types (A) and (B), Scheme 5].

The peaks for the ions (A) and (B) are characterised by having the maximum intensity in the majority of spectra.[79]

Scheme 5



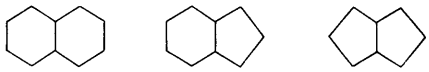
Analysis of the spectra of deuterated analogues of compound (VI) permitted the conclusion that the formation of the ions (A) and (B) involves the ionisation of the most highly substituted cyclopropane bond with localisation of the positive charge on the most substituted carbon atom.[79]

IV. BICYCLIC SATURATED HYDROCARBONS

1. Hydrocarbons with a Condensed Type of Junction between the Rings

(a) Unsubstituted hydrocarbons. In the series of compounds of this type attention has been concentrated on the mass spectra of hydrocarbons consisting of five- and/or six-membered rings belonging to the bicyclo[4.4.0]decane (VII),

bicyclo[4.3.0]nonane (VIII), and bicyclo[3.3.0]octane (IX) series.[2,31,80–86] Data have been published also for the spectra of hydrocarbons with cyclopropane (X) and cyclobutane (XI) rings.[86–93]

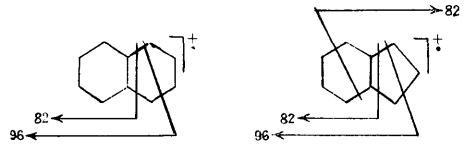


(VII) (VIII) (IX)

The stability of the MI of the bicycloalkanes considered decreases in the sequence (VII) > (VIII) > (IX) in parallel with the increased strain in the molecules.[80–82] In contrast to the spectra of unsubstituted monocyclic hydrocarbons, the intensity of the peak due to the ion $[M-CH_3]^+$ in the spectra of compounds (VII)–(IX) is low. In the case of compounds (VIII) and (IX) the abstraction from the molecular ion of a fragment containing two carbon atoms takes place mainly in the form of the ethylene molecule. This process is not characteristic of compounds (VII). The ratio of the ionic species $[M-C_3H_6]^{+\cdot}$ and $[M-C_3H_7]^+$ is influenced by the number of methylene units in the ring. Thus the presence of only cyclopentane rings in the molecules of compounds (IX) entails the preferential elimination of a three-carbon fragment in the form of the propyl radical; the intensity of the peak for the ion $[M-C_3H_7]^+$ becomes a maximum§, much greater than the intensity of the peak in the ionic species $[M-C_3H_6]^{+\cdot}$. In the case of the hydrocarbon (VII), containing only cyclohexane rings, there is a high probability of the elimination of a propene molecule and the ratio of the intensities of the above peaks changes ($I_{[M-C_3H_6]^{+\cdot}} > I_{[M-C_3H_7]^+}$). On the other hand, for the molecules of compounds (VIII), consisting of five- and six-membered rings, the peaks of the ionic species $[M-C_3H_6]^{+\cdot}$ and $[M-C_3H_7]^+$ (*m/z* 82 and 81 respectively) have similar intensities and their ratio depends on the type of junction between the rings: $I_{82} > I_{81}$ for *trans*-(VIII), while the opposite relation obtains for *cis*-(VIII).

The differences between the thermochemical stabilities of the *cis*- and *trans*-isomers of compounds (VII) and (VIII) [compounds (IX) exist solely as the *cis*-isomers[94]] are clearly reflected in their spectra.[80–84] Thus a much higher intensity of the MI peak and a lower intensity of the peaks due to the primary ions are observed in the spectra of the more stable *trans*-isomers of compounds (VII) and (VIII) compared with the spectra of the *cis*-isomers. With decrease in the energy of the ionising electrons, the above differences become more pronounced.

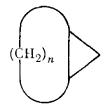
Interesting results have been obtained from the comparison of the IE and AE of the *cis*- and *trans*-isomers. The IE of the molecular ions for the two isomers proved identical but the AE of some of the ions (*m/z* 96, 82) are higher for the *trans*-isomers, while those for other ions (*m/z* 95, 68, 67) are higher for the *cis*-isomers. The AE measured with a high accuracy can be used to determine the differences between the enthalpies of formation of the *cis*- and *trans*-isomers of compounds (VII) and (VIII).[95] The difference between the ΔH of the stereoisomers should then be correlated quantitatively to the differences between the AE of only those ions which are formed from the MI in a single stage as a result of simple bond rupture. From this standpoint, the ions with *m/z* 96 and 82 are of greatest interest:



(VII) (VIII)

The equality of the differences between the AE and ΔH for the stereoisomers of compounds (VII) and (VIII) is observed only for the ion with *m/z* 96. The absence of such clear-cut quantitative correlation for the ion with *m/z* 82 can be associated with the difference between the pathways leading to its formation on decomposition of the stereoisomers, while for other ions it can be associated with the fact that they are in the nature of rearrangements (*m/z* 109, 95, 81) or with the multistage character of their formation (*m/z* 67. 68).[95]

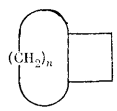
The differences between the spectra of hydrocarbons of type (X) are associated with the size of the polymethylene ring:[87–91]



(X); n = 3-10

The stability of the MI decreases from 11 to 0.5% with increase of the size of this ring from $n = 3$ to $n = 8$ and then increases slightly. The decomposition of the MI of hydrocarbons (X) takes place as a result of the simultaneous occurrence of two processes—the contraction of the polymethylene ring and the opening of the cyclopropane ring.[87] The intensity of the peak due to the ion $[M-CH_3]^+$ is a maximum in the spectrum of bicyclo[3.1.0]hexane and diminishes with increase of the size of the larger ring. Comparision of the spectra of compounds (X) and their halogeno-derivatives suggests[87] that the methyl radical split off from the MI is derived from a methylene unit of the three-membered ring. The peak of the ion $C_5H_7^+$ with *m/z* 67 shows the maximum intensity in the majority of the spectra.

Bicyclo[*n*.2.0]alkanes (XI) are characterised by a low stability of the MI (1.6–0.2%) and, in contrast to bicyclo-[*n*.1.0]alkanes (X), the stability of their MI is independent of the size of the larger ring of the molecule.[92,93]



(XI); n = 2–6

On the other hand, the intensity of the peak due to the ion $[M-CH_3]^+$ diminishes with increase in the size of the above ring. The MI of the bicycloalkanes (XI) decompose with the preferential cleavage of the C–C bonds in the cyclobutane ring, while the intensity of the peak of the radical-ion $[M-C_2H_4]^{+\cdot}$, formed as a result of this process, is a maximum in the majority of the spectra.

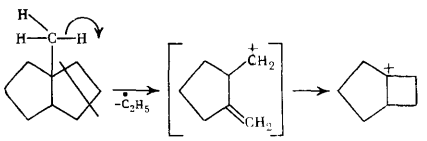
(b) Monosubstituted hydrocarbons. The mass spectra of a large number of structural and geometrical isomers of the methyl derivatives of compounds (VII)–(IX) have been described in the literature.[65,85,86,96,97] It has been observed that the MI of methylbicyclo[4.4.0]decanes (XII) are more resistant to electron impact than the MI of methylbicyclo-[4.3.0]nonanes (XIII) and methylbicyclo[3.3.0]octanes (XIV). In the series of structural isomers of compounds (XIII) and (XIV) the greatest stability of the MI is observed for the

§There is a possibility of a two-stage pathway to the formation of the ion $[M-C_3H_7]^+$—from the radical-ion $[M-C_2H_4]^{+\cdot}$ or the ion $[M-CH_3]^+$.

angular position of the methyl group.[85,86] The spectra of compounds (XII) with angular substituents have not been described.

The introduction of the methyl group into the molecules, of the unsubstituted hydrocarbons (VII)–(IX) does not entail significant changes in the intensity of the MI peak. The intensity of the peak of the ion $[M-CH_3]^+$ in the spectra of compounds (XII)–(XIV) is higher compared with that observed in the spectra of compounds (VII)–(IX), the only exception being 7-methylbicyclo[4.3.0]nonane. The intensity of the $[M-CH_3]^+$ peak then changes markedly as a function of both the position of the substituent and the stereochemistry of the molecule.

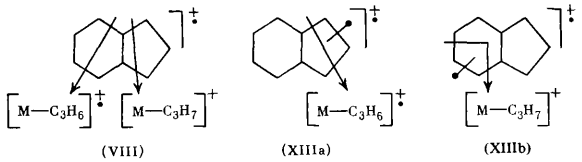
The abstraction from the MI of a fragment consisting of two carbon atoms takes place in the case of hydrocarbons (XIII)–(XIV) mainly in the same manner as in the unsubstituted structures—in the form of the ethylene molecule. The fact that the elimination of the ethyl radical from structures with angular substituents is favoured by energy factors has been explained[85,86] by the disposition of the methyl group convenient for the migration of a proton:



(XIV) *m/z* 95

The abstraction of a two-carbon fragment from the molecular ion is not characteristic of compounds (XII).

The main pathways leading to the fragmentation of the MI of methylbicycloalkanes (XII)–(XIV) are associated with the rupture of the bond at the tertiary (quaternary) carbon atoms.[85,86,96] The peaks of the ionic species $[M-C_4H_8]^{+\cdot}$, $[M-C_4H_9]^+$, $[M-C_5H_{10}]^{+\cdot}$, and $[M-C_5H_{11}]^+$ are the most intense in the spectra of compounds (XII), while the $[M-C_3H_6]^{+\cdot}$ and $[M-C_3H_7]^+$ peaks are the most intense in the spectra of compounds (XIII)–(XIV). The ratio of the latter peak intensities depends on the position of the methyl group in the cyclopentane or cyclohexane ring of the molecule: for structures with the substituent in the cyclopentane ring [structures (XIIIa)], a propene molecule is eliminated preferentially, while the presence of a substituent in the cyclohexane ring [structures (XIIIb)] promotes the ejection of a propyl radical from the MI¶. As a consequence, the ratio $I_{[M-C_3H_6]^{+\cdot}}/I_{[M-C_3H_7]^+}$ becomes diagnostic: it is greater than unity for compounds (XIIIa) and less than unity for compounds (XIIIb).



(VIII) (XIIIa) (XIIIb)

The differences between the spectra of the *cis*- and *trans*-isomers of compounds (XII)–(XIV) are correlated with their relative stabilities.[85,86,96] Thus a more stable MI is formed also in the case of the more stable bicycloalkane stereoisomers. The abstraction of the methyl substituent from the MI proceeds as a rule also more vigorously for the more stable stereoisomers, while an increase of strain in the molecules entails an increase of the contribution by the competing dissociation of endocyclic bonds. The attempt to explain these differences for the stereoisomers of compounds (XII) as a consequence of the stronger decomposition of the ion $[M-CH_3]^+$ in the case of the less stable isomer[65] appears little justified, since the difference between the enthalpies of the stereoisomers influences mainly the rates of the primary and not secondary MI decomposition reactions[98]—those which can result in an excess of internal energy, which is characteristic of the less stable isomer. The features discussed above are more likely to be a consequence of differences between the energy relations of the competing MI decomposition reactions. For the less stable isomer with an axial methyl group, the decomposition of the cyclic system consuming less energy obtains more readily, while in the case of the more stable stereoisomers with an equatorial substituent the probability of the rupture of the exocyclic bond increases, which results in an increase of the peak intensity of the ion $[M-CH_3]^+$ in its spectrum. If the radial abstraction process were energetically more favourable than the cleavage of the ring, the peak of the ion $[M-R]^+$ in the spectrum of the stable isomer would have had a greater intensity.

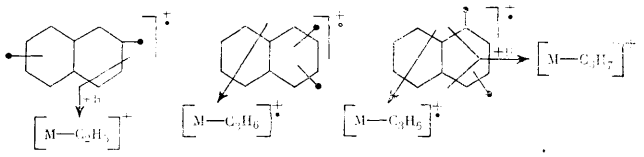
In order to confirm this hypothesis, studies were made of the mass spectra of ethylbicyclo[4.4.0] decanes,[98] because the dissociation energy of the $C-C_2H_5$ exocyclic bond is much lower than that of the $C-CH_3$ bond. Indeed the peak intensity of the ion $[M-C_2H_5]^+$ in the spectra of ethylbicyclo[4.4.0]decanes is much higher than the peak intensity of the ion $[M-CH_3]^+$ in the spectra of compounds (XII) and the differences between their intensities in the spectra of the stereoisomers are reduced, as was to be expected. Nevertheless, this peak still remains more intense in the spectrum of the stereoisomer with an equatorial ethyl group.

The measurements of the IE and AE for the ions of 2- and 3-methylbicyclo[4.4.0]decanes with a *trans*-junction between the rings also failed to throw light on the above equation.[97]

(c) Disubstituted hydrocarbons. The spectra of dimethylbicycloalkanes have been studied in detail only for compounds (VII).[99–101] In addition, the spectra of 7,7-, and 7,9-, and 1,9-dimethyl derivatives of compounds (VIII)[85,102] and the 1,2-, 1,3-, 2,4-, and 3,7-dimethyl derivatives of compounds (IX)[86] have been described. The stability of the MI of dimethylbicycloalkanes with angular substituents is higher than that of the MI of all the methyl-substituted compounds (XII)–(XIV), while for the remaining dimethyl derivatives it is lower than for compounds (XII)–(XIV). The peak intensity of the ion $[M-CH_3]^+$ varies within broad limits. The presence of a geminal group leads to a sharp increase in the intensity of this peak, with the exception of 7,7-dimethylbicyclo[4.3.0]nonane, while the angular position of one of the methyl groups has little influence on its magnitude.

The decomposition of the cyclic system takes place preferentially via the rupture of the bonds at the tertiary and quaternary carbon atoms. The abstraction of a two-carbon fragment from the MI of dimethylbicyclo[4.4.0]decane (XV) takes place mainly in the form of a radical from the substituted ring of the molecule, while the peak intensity of the ion $[M-C_2H_5]^+$ is greatest in the spectra of structures of type (XVa) in which the disposition of the substituents is favourable for this purpose. On the other hand, the peak of the ion $[M-C_2H_5]^+$ is virtually absent from the mass spectra of compounds (XV) with angular and geminal substituents:

¶ The opposite ratio of the intensities of these peaks has been observed for unsubstituted structures on decomposition of the rings in compounds (VIII).



M, (XVa) M, (XVb) M, (XVc)

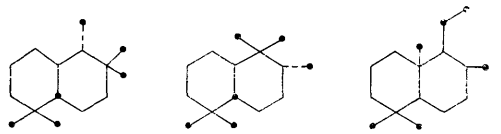
C_9 ions are present in the spectra of all dimethylbicyclo-[4.4.0]decanes. For structures of type (XVb), where both substituents are in the same ring, the peak intensities of these ions are comparatively low and that of the radical-ion $[M-C_3H_6]^+$ is somewhat greater than that of the ion $[M-C_3H_7]^+$, as in the spectra of unsubstituted compound (VII). It has been suggested[100] that the formation of the radical-ion $[M-C_3H_6]^+$ is associated with the cleavage of the unsubstituted ring. This hypothesis is supported by the higher peak intensity of the ion $[M-C_3H_7]^+$ compared with that of $[M-C_3H_6]^+$ in the spectra of 2,4- and 2,5-dimethylbicyclo[4.4.0]decanes (XVc), which also have one unsubstituted ring, but the disposition of the methyl groups in the second ring is favourable for the elimination of the C_3H_6 and C_3H_7 fragments.

The formation of C_8 (m/z 109, 110) and C_7 (m/z 95, 96) ions takes place most vigorously for the hydrocarbons (XV); the corresponding peaks have as a rule the maximum intensity in the spectra. Geminally substituted structures, in the spectra of which the peak of the ion $[M-CH_3]^+$ predominates, are an exception. Structures of type (XVb) are distinguished by a higher peak intensity of the ions $[M-C_4H_9]^+$ compared with those of $[M-C_4H_8]^+$ ($I_{109} \gg I_{110}$). For hydrocarbons with a different disposition of the methyl groups in the molecule, the ratio of these peaks is reversed to a marked extent ($I_{109} \ll I_{110}$). The peaks of C_7 ions have a high intensity in the spectra of all the structural isomers with the exception of 2,5-dimethylbicyclo[4.4.0]decane, for which their formation in a single stage is impossible without skeletal rearrangement.[99]

As a consequence of the limited number of spectra of dimethyl derivatives of compounds (VIII) and (IX), it is difficult to isolate any group characteristics of the structural isomers.[82,85] One can only note that the presence or absence of an angular methyl group in the molecule can be inferred from the ratio of the peak intensities of the ionic species $[M-C_3H_7]^+$ (m/z 95) and $[M-C_3H_6]^+$ (m/z 96) in the spectra of dimethyl derivatives of compound (IX): $I_{95}/I_{96} > 1$ for the 1,2- and 1,3-dimethyl derivatives and $I_{95}/I_{96} < 1$ in the absence of a substituent at C(1).

In the series of dimethylbicycloalkane stereoisomers examined the same dependence of the MI intensity on the stability of the molecule is observed as for the monosubstituted structures: in the mass spectrum of the sterically less hindered stereoisomer the peaks of the ionic species M^+ and $[M-CH_3]^+$ are as a rule more intense than those observed in the spectra of the more hindered isomer. The differences between the peak intensities of the primary ions in the series of stereoisomers of certain hydrocarbons are then found to be sufficiently large to be employed for diagnostic purposes.[85,86,99-102]

(d) Polyalkyl-substituted hydrocarbons. The mass spectra of compounds having more than two substituents in the molecule are known only for the most stable bicyclo[4.4.0]decane system—compounds (XV)–(XVII).[103-105]



(XVI) (XVII) (XVIII)

The difference between the positions of the geminal and methyl groups in the molecules of the structural isomers of compounds (XVI) and (XVII) does not affect the character of the decomposition of their molecular ions—the spectra of compounds (XVI) and (XVII) proved to be similar:[103] they are both characterised by a low-intensity peak of the molecular ion (m/z 208) and the maximum peak intensity of the ion $[M-CH_3]^+$. Fragments corresponding to the abstraction of two and three carbon atoms from the molecular ion are absent. Despite the presence of the geminal group in the molecule of compound (XVIII), its mass spectrum is characterised by a small peak due to the ion $[M-CH_3]^+$ and an intense MI peak (m/z 222).[105] The peak intensity for the ion $[M-C_2H_5]^+$ is also high and the peak for the ion with m/z 123 has the highest intensity.

2. Hydrocarbons with a Bridge Type of Junction between the Rings

(a) Unsubstituted hydrocarbons. The vast majority of the mass spectra quoted in the literature[91,106-119] refer to hydrocarbons consisting of five–six-membered rings [compounds (XIX)–(XXII)]. The only exception is bicyclo[1.1.1]-pentane (XXIII),[120] whose mass spectrum contains, apart from the MI peak with the maximum intensity, also the peak of the ion $[M-H]^+$. The study of the decomposition of the deuteriated analogue of compound (XXIII) led to the conclusion that hydrogen is eliminated not only from the methylene but also from the methylidyne unit. The peak intensities of the remaining fragment ions are low.



(XIX) (XX) (XXI) (XXII) (XXIII)

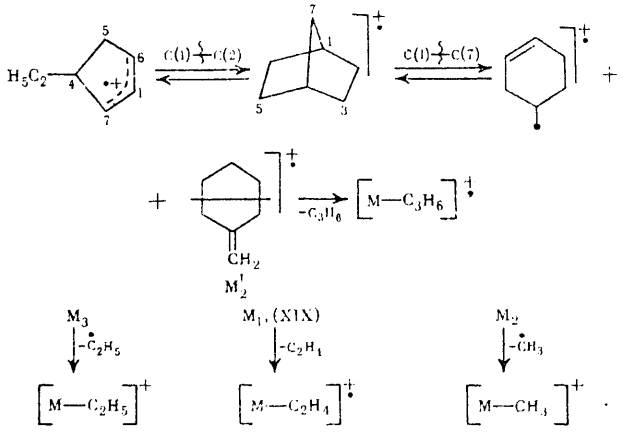
Table 4.

Compound	$I_{[M]^+}$	$I_{[M-CH_3]^+}$
(XIX)	3.8	14.7
(XX)	7.5	3.9
(XXI)	11.9	0.5
(XXII)	12.3	3.3

The stability of the MI and the ion $[M-CH_3]^+$ in the spectra of the unsubstituted bicycloalkanes (XIX)–(XXII) varies within wide limits (Table 4).[106,108,117,119] A molecule of the hydrocarbon (XIX) is subject to an intense strain arising as a consequence of the distortion of the C(1)–C(7)–C(4) angle (~90°) and an appreciable "Pitzer" interaction between the hydrogen atoms [C(2), C(3) and C(5), C(6)], which is characteristic of a six-membered ring in the boat conformation. Under the conditions of electron impact, these difficulties initiate the formation of isomeric forms of the molecular

ion (M_2 and M_3, Scheme 6), whose subsequent decomposition leads to the appearance of the intense peaks of $[M-CH_3]^+$ and $[M-C_2H_5]^+$ (maximum peak).[117,118] The decomposition of the form M_1 leads to the appearance of the intense peak of the radical-ion $[M-C_2H_4]^{+\cdot}$.

Scheme 6



In the spectra of the hydrocarbons (XX) and (XXII), whose molecules also contain the dimethylene bridge, the peak of the ion $[M-C_2H_5]^+$ is one of the most intense. In the spectra of compounds (XX)–(XXII) the maximum intensity is shown by the peak of the ion $[M-C_3H_7]^+$. For compound (XX), the formation of this ion is attributed to the successive elimination of a methyl radical and an ethylene molecule from the MI,[106] in the case of compound (XXI) it is believed to arise as a consequence of the ejection of a propyl radical from the monocyclic form of the MI,[119] while for compound (XXII) the formation of the ion is believed to be due to the contributions of both decomposition pathways.[108]

Table 5. The peak intensities of the characteristic ions in the spectra of monomethylbicycloalkanes.[106,108,117–119]

Ions	(XIX)	(XX)	(XXI)	(XXII)
M^+	2.0—4.2	1.5—6.7	5.0—8.6	10.1—11.1
$[M-CH_3]^+$	5.8—9.8	2.7—12.8	3.2—18.1	4.3—10.8
$[M-C_2H_5]^+$	10.6—32.5	3.7—28.6	0.4—5.4	13.8—22.5
$[M-C_3H_7]^+$	9.5—16.6	3.2—24.3	3.8—32.2	7.3—12.8
$[M-C_4H_9]^+$	—	6.3—14.6	7.3—14.9	9.8—14.3

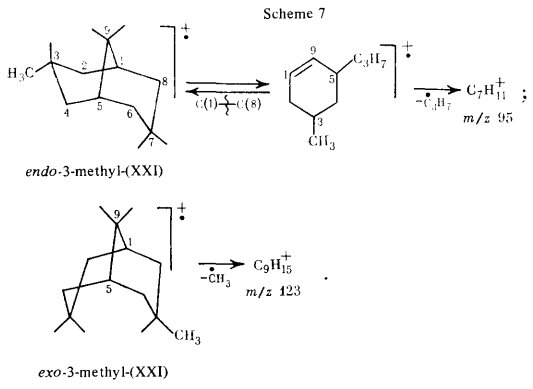
(b) Monosubstituted hydrocarbons. The introduction of the methyl substituent into the molecules of compounds (XIX)–(XXII) lowers somewhat the stability of their MI. The highest stability of the MI is then shown for bicyclo[2.2.2]octanes (Table 5), which makes it possible to distinguish them from the isomeric bicyclo[3.2.1]octanes.[106–108,112,117–119] The peak intensity of the ion $[M-CH_3]^+$ derived from the methyl derivative of compound (XXII) is higher compared with the unsubstituted structure; nevertheless the ratio $I_{[M]^+}/I_{[M-CH_3]^+}$ remains greater than unity. For the remaining members of the series, the ratio of the intensities of these peaks is determined by the position of the methyl group in the molecule.

The decomposition of the cyclic components of the bridged bicyclo-octanes takes place preferentially with the abstraction from the molecular ion of fragments containing two and three carbon atoms. A two-carbon fragment is ejected mainly as a result of the decomposition of the unsubstituted dimethylene bridge. This process proceeds very vigorously for the methyl derivatives of compounds (XIX), (XX), and (XXII), with the exception of 6-methylbicyclo[3.2.1]octane, but is not characteristic of compounds (XXI) (Table 4). A distinctive feature of the spectra of the 6- and 8-methyl derivatives of compound (XX), in which the substituent is attached to the most strained part of the molecule, is the prominance of the peak due to the primary odd-electron ionic species, namely $[M-C_3H_6]^{+\cdot}$ and $[M-C_2H_4]^{+\cdot}$ respectively, whose intensity in the spectra of the remaining structural isomers does not exceed 50% of the maximum value.

The monosubstituted hydrocarbons (XIX)–(XXI) exist in the form of two (*exo*- and *endo*-) geometrical isomers, apart from compounds (XIX)–(XXI) substituted in the angular position. As a consequence of the high symmetry of the molecule of hydrocarbon (XXII), its monosubstituted derivatives have no geometrical isomers. The stereochemical characteristics of the molecules are reflected in the spectra of the stereoisomers differing greatly in their thermochemical stabilities. These differences are particularly clear in the spectra of the *exo*- and *endo*-isomers of the 3-methyl derivative of compound (XXI).[119] The molecule of compound (XXI) exists in the "chair–chair" conformation, in which there is a strong *trans*-annular interaction with the axial hydrogen atoms at C(3) and C(7) and for this reason the additional interactions in the molecule, arising following the introduction of substituents [in particular, the interaction of the 3-*endo*-methyl group with the hydrogen atom at C(7) in the molecules of 3-methyl substituted derivatives], force one of the rings to adopt the boat conformation.

Thus the decomposition of the MI of the *endo*-epimer is determined by the removal of the "bowsprit" interactions, which is achieved, according to the authors,[119] by the efficient formation of the isomeric monocyclic form of the MI. The subsequent decomposition of this form yields the ion with *m/z* 95, the peak intensity of which is a maximum in the spectrum. The main pathway in the decomposition of the *exo*-epimer involves the elimination of the methyl group. The peak of the ion $[M-CH_3]^+$ in its spectrum has the maximum intensity (Scheme 7).

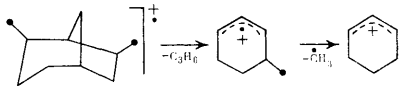
Scheme 7



(c) Disubstituted hydrocarbons. The introduction of a second methyl group into the molecules of compounds (XIX)–(XX) and (XXII) reduces somewhat the stability of the MI.[106,108,117] In the case of compound (XXI) it hardly changes.[119] On the other hand, no regularity is observed in the variation

of the peak intensity of the ion $[M-CH_3]^+$ and the ratio $I_{[M]^+}/I_{[M-CH_3]^+}$ in a series of structural isomers. The peaks of the ionic species $[M-C_2H_5]^+$, $[M-C_3H_7]^+$, and $[M-C_4H_8]^{+\cdot}$ are the most intense in the spectra of the dimethyl derivatives of compounds (XIX)–(XXI) and one of these actually has the maximum intensity. Analysis of the mass spectra of structural isomers available in the literature does not allow unambiguous conclusions about the structural elements of the molecule (such as the structure of the bicyclic skeleton, substitution in one or different rings, and vicinal or geminal disposition of the methyl groups).

However, the spectra of hydrocarbons (XIX) and (XX) substituted in the angular position stand out somewhat. They are as a rule characterised by a considerable predominance of one [the 1,2-, 1,6-, and 1,7-dimethyl derivatives of compound (XX) and the 1,4-dimethyl derivative of compound (XIX)] or two [the 1,3-, 1,4-, and 1,5-dimethyl derivatives of compound (XX) and the 1,2- and 1,3-dimethyl derivatives of compound (XIX)] decomposition pathways as a result of the preferential rupture of the bond at the quaternary carbon atom. The intensities of the peaks of the remaining ions under these conditions do not exceed 25% of the intensity of the main peak. An exception is provided by the 1,8-dimethyl derivative of compound (XX), which is characterised by an intense decomposition of the molecular ion to an equal extent via all the pathways as a consequence of the considerable strain in the molecule. For the remaining dimethyl derivatives of hydrocarbon (XX), each having three tertiary carbon atoms, the fragmentation of the molecular ion proceeds with equal probability via several pathways; according to some investigators[106] the methyl substituents are retained in the charged fragments and their subsequent abstraction leads to the strong formation of secondary ions.



In the series of geometrical isomers of dimethylbicyclooctanes the spectrum of the most stable stereoisomer of each structure also exhibits the most intense peaks of the ions M^+ and $[M-CH_3]^+$. In other respects the spectra of the stereoisomers are very similar.[106,108,117–119]

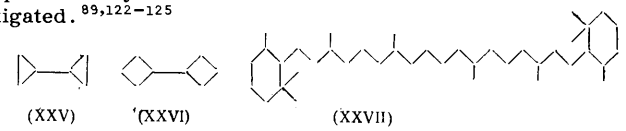
3. Other Bicyclic Systems

(a) Spiran hydrocarbons. Spiropentane (XXIV) is the only representative of this class whose mass spectrum has been described.[2,121]


(XXIV)

It is of interest that at 70 eV the peak of the ion $(M-H)^+$ is the most intense in the spectrum of compound (XXIV), while at 15 eV the peak of the radical-ion $(M-C_2H_4)^{+\cdot}$ is the most intense. The intensity of the peak for the ion $(M-CH_3)^+$ is low in both spectra.

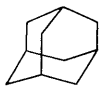
(b) Hydrocarbons with single-bonded rings. The mass spectra of hydrocarbons of this class have been little investigated.[89,122–125]


(XXV) (XXVI) (XXVII)

The MI peak in the spectra of compounds (XXV)–(XXVII) is insignificant. The strongest peak in the spectra of bicyclopropyl (XXV) [89] and bicyclobutyl (XXVI) [122] {the radical-ions $[M-C_2H_4]^{+\cdot}$ and $[M-C_3H_6]^{+\cdot}$} corresponds to the ionic species formed on dissociation of endocyclic bonds at a tertiary carbon atom. The strongest peak in the spectrum of perhydro-β-carotene (XXVII) is that of the secondary ion with m/z 69.[123–125] The height of the peak due to the ion $[M-CH_3]^+$ is considerable (90% of the maximum value) only in the spectrum of compound (XXV).

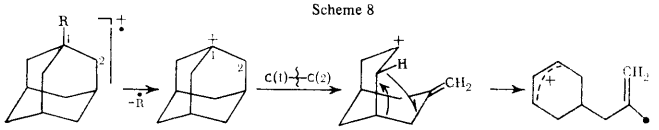
V. TRICYCLIC SATURATED HYDROCARBONS

The greatest number of studies on the mass spectrometry of tricyclic hydrocarbons have been devoted to compounds of the adamantane series. Adamantane (XXVIII) itself is the first among tricyclic hydrocarbons to have been identified in petroleums; much attention has been devoted to hydrocarbons of the adamantane series in the chemistry of petroleum.[126] The adamantane system is the most stable among tricyclic systems, which is due to the absence of any internal strains, since all three rings have the chair conformation. In the spectrum of compound (XXVIII) the MI peak has the maximum intensity. The easiest decomposition reaction of the MI of adamantane involves the elimination from it of fragments containing three and four carbon atoms, but the peak intensities of the ions formed do not exceed 50% of the maximum value:[127]


(XXVIII)

Regardless of the energy of the ionising electrons, the decomposition of the MI of alkyladamantanes leads to the formation of the adamantyl ion $C_{10}H_{15}^+$ with m/z 135 [Scheme 8, ion (C)] from the monoalkyl derivative of compound (XXIX) [128–132] or of its homologues from polyalkyladamantanes.[132–134] The peaks of these ions have the maximum intensity. It has been suggested[130,133] that the ion (C) does not retain the tricyclic structure with a positive charge on the carbon atom at the bridgehead but actually undergoes an extensive rearrangement to the cyclic allyl ion (D) which accounts for its high stability.

Scheme 8

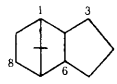


Examination of the mass spectra of 1- and 2-alkyladamantanes demonstrated a considerable decrease in the stability of the MI with increase in the length of the substituent group[128,129,132] and, for the same length of the substituent group, the stability of the MI is higher for the 2-substituted structures than for the 1-substituted structures. As a result, the ratio $I_{[M]^+}/I_{[M-R]^+}$ can be used as a criterion in determining the position of the substituent in the adamantane nucleus: it is 5–7 times higher for the 2-substituted derivatives than for the 1-substituted derivatives.

An increase in the number of substituents in the adamantane molecule leads to a decrease of the stability of the MI and an increase of the peak intensity of the ion $[M-R]^+$.[129, 132,133] In contrast to the spectra of monomethyladamantanes, the peaks of the ions $[M-C_2H_5]^+$ appear in the spectra of the tri- and tetrasubstituted derivatives, which indicates,

according to the authors,[129] the additional elimination of the CH_2 fragment from the other methyl group. The peak intensity of the above ion increases with increased number of methyl groups in the molecule.

Apart from the mass spectrum of adamantanes, a detailed study has been made of the spectrum of the isomeric tricyclo[5.2.1.$0^{2,6}$]decane (XXX) and its methyl and ethyl derivatives,[135,136] for which the IE have been measured.[137]

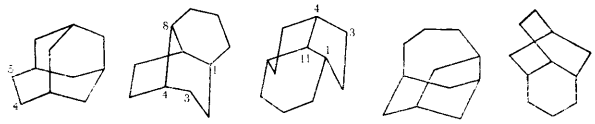


(XXX)

The peak for the ion $[M-C_3H_5]^+$ with *m/z* 95, formed following the abstraction of the CH_2=CH−CH_2 fragment from the MI, has the maximum intensity in the spectra of the *exo*- and *endo*-isomers of compound (XXX).

The introduction of a substituent into the molecule of compound (XXX) (the 3-, 4-, 8-, and 10-methyl derivatives have been studied) decreases the stability of the MI. On the other hand, the peak intensity of the ion $[M-CH_3]^+$ increases relative to that noted for the unsubstituted structure. The peak for the ion $[M-C_2H_5]^+$ has the maximum intensity only in the spectrum of 10-methyltricyclo[5.2.1.$0^{2,6}$]-decane. Apparently it arises in the spectrum of this compound via a mechanism analogous to that described for 7-substituted bicyclo[2.2.1]heptanes.[118] In all the remaining spectra the peaks of the secondary ions have the maximum intensities.[135,136]

As regards tricyclic hydrocarbons having the composition $C_{11}H_{18}$ (tricycloundecanes), there exist literature data for a fairly large number of structures,[138–145] many of which have been identified in petroleum.[146] The mass spectrum of homoadamantanes (XXXI) resembles that of adamantane—the MI peak is more than twice as intense as the remaining peaks in the spectrum.[138] The main difference between the spectra of compounds (XXVIII) and (XXXI) is associated with the presence in the latter of the intense peak of the ion $[M-CH_3]^+$. The spectra of the hydrocarbon labelled with ^{13}C have shown[139] that each atom in the C(4)−C(5) dimethylene bridge is involved in the abstraction of the methyl group from the MI to the extent of ~25%.



(XXXI) (XXXII) (XXXIII) (XXXIV) (XXXV)

The maximum intensity of the MI peak is observed in the spectrum of tricyclo[5.4.0.$0^{4,8}$]undecane (XXXII),[140] but a high intensity of the main fragment ions is also characteristic of this compound. The decomposition of the MI of tricyclo[5.3.1.$0^{4,11}$]undecane (XXXIII) takes place with the preferential ejection of an ethylene molecule.[140] The molecule of 4-homoprotoadamantane (XXXIV), containing the cycloheptane ring, decomposes via many pathways under electron impact.[141] The peak of the secondary ion $[C_6H_7]^+$ with *m/z* 79 has the maximum intensity in its spectrum.

Among the hydrocarbons having the composition $C_{11}H_{18}$, the most interesting is tricyclo[5.3.1.$0^{3,8}$]undecane—homoisotwistane (XXXV).[142–144] This hydrocarbon is the only one among the tricycloundecanes investigated which is formed solely from six-membered rings and the valence angles in its molecule are completely undistorted. The characteristics of the structure of homoisotwistane are reflected in its high thermal stability[104] and the high intensity of the MI peaks in its spectrum, which exceeds by a factor of almost two the intensities of the remaining peaks. The maximum intensity of the MI peak persists also in the spectrum of 1-methyltricyclo[5.3.1.$0^{3,8}$]undecane,[145] which is not characteristic of methyl-substituted saturated hydrocarbons.

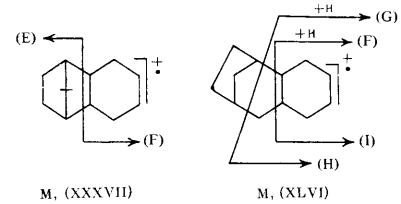
Systematic mass-spectrometric studies of a series of unsubstituted tricycloundecanes[144] and tricyclododecanes,[147] made up of five- and six-membered rings, demonstrated the possibility of identifying structural and in many instances also geometrical isomers. The mass spectra of tricyclo-[6.3.0.$0^{2,6}$]undecane (XXXVI), tricyclo[6.2.1.$0^{2,7}$]undecane (XXXVII), tricyclo[5.2.2.$0^{2,6}$]undecane (XXXVIII), tricyclo-[5.3.1.$0^{2,6}$]undecane (XXXIX), tricyclo[6.2.1.$0^{2,6}$]undecane (XL), tricyclo[5.3.1.$0^{3,7}$]undecane (XLI), tricyclo-[6.2.1.$0^{1,6}$]undecane (XLII), tricyclo[5.2.2.$0^{1,5}$]undecane (XLIII), tricyclo[6.3.0.$0^{1,5}$]undecane (XLIV), tricyclo-[7.3.0.$0^{3,8}$]dodecane (XLV), tricyclo[7.2.1.$0^{2,7}$]dodecane (XLVI), tricyclo[6.3.1.$0^{2,6}$]dodecane (XLVII), tricyclo-[6.2.2.$0^{2,7}$]dodecane (XLVIII), tricyclo[6.3.1.$0^{4,12}$]dodecane (XLIX), tricyclo[7.2.1.$0^{1,6}$]dodecane (L), tricyclo[6.3.1.$0^{1,6}$]-dodecane (LI), tricyclo[6.3.1.$0^{1,5}$]dodecane (LII), and tricyclo[5.3.1.$1^{4,11}$]dodecane (LIII) have been investigated.

The stability of the MI of the tricyclanes investigated varied within wide limits (1.8–13.3%) and is lower the greater the number of cyclopentane rings in the molecule. The mass spectra of all the tricyclanes contain the peaks of the ions $[M-CH_3]^+$ and $[M-C_2H_5]^+$, the intensity of the latter being particularly high in the spectra of compounds containing the dimethylene bridge. The abstraction of a three-carbon fragment from the MI takes place strongly only in the decomposition of tricyclododecanes.

All the hydrocarbons (XXXV)–(LIII) investigated can be divided into two groups according to the absence (group 1) or presence (group 2) of a carbon atom common to all three rings. The quantitative differences between the spectra of the hydrocarbons in groups 1 and 2 reflect the fundamental difference between the pathways in the decomposition of their MI.

The first significant difference for tricycloundecanes consists in the peak intensity for the ion $C_5H_7^+$ with *m/z* 67 [ion (E), Scheme 9], which is more than twice as high in the spectra of the group 1 hydrocarbons (XXXVI)–(XL) as in the spectra of the group 2 compounds (XLI)–(XLIV). This is apparently associated with the fact that the formation of the ion (E) from compounds (XXXVI)–(XL) requires the rupture of two C−C bonds (Scheme 9, on the left), while in compounds (XLI)–(XLIV) three such bonds must be broken, which is less probable.

Scheme 9



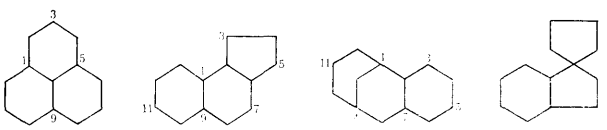
M, (XXXVII) M, (XLVI)

The second difference is the absence from the spectra of group 2 hydrocarbons of the peak of the ion $C_6H_{11}^+$ with *m/z* 83 [ion (F)]. In the case of group 1 hydrocarbons this ion is formed directly from the molecular ion. Among group 2 hydrocarbons, its formation requires, apart from the rupture of the C−C bonds, the migration of at least one hydrogen atom to the C_6 fragment. The impossibility of such migration for steric or other reasons apparently leads

to the absence of the peak of the ion (F) from the spectra of group 2 hydrocarbons.

The spectra of group 1 tricyclododecanes (XLV)–(XLVIII) contain intense peaks for the ionic species $C_6H_{11}^+$ (m/z 83), $C_7H_{13}^+$ (m/z 97), $C_7H_{12}^+$ (m/z 96), and $C_6H_{10}^+$ (m/z 82) [ionic species (F), (G), (H), and (I), Scheme 9, on the right], whereas in the spectra of group 2 hydrocarbons the first two peaks are missing and the intensities of the last two are insignificant. The above differences are associated with the impossibility of the formation of these ions as a result of the simple rupture of two bonds in the molecules of group 2 hydrocarbons. Their formation following the dissociation of three bonds, is firstly, less favourable on energy grounds and, secondly, requires the migration of at least one hydrogen atom.

The mass spectra of tricyclic hydrocarbons having the composition $C_{13}H_{22}$ have been obtained for tricyclo[7.3.1.$0^{5,13}$]-tridecane (LIV),[107] tricyclo[7.4.0.$0^{2,6}$]tridecane (LV),[148] tricyclo[7.3.1.$0^{2,7}$]tridecane (LVI),[149] and 1,2-tetramethylene-spiro[4,4]nonane (LVII).[148]



(LIV) (LV) (LVI) (LVII)

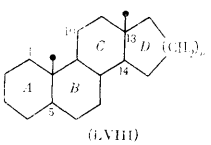
The intensity of the MI peak for the first three compounds is high, while that of the peaks for the ions $[M-CH_3]^+$ and $[M-C_2H_5]^+$ is insignificant. The main pathway in the decomposition of the MI of compounds (LIV)–(LVIII) involves the abstraction of fragments containing three carbon atoms: in the spectra of compounds (LV) the peak of the ion $[M-C_3H_7]^+$ has the maximum intensity. The mass spectrum of the hydrocarbon (LVII) is characterised by a high peak intensity of the ion $[M-C_4H_9]^+$ greatly exceeding that observed for the remaining peaks in the spectrum.

VI. HYDROCARBONS WITH FOUR AND MORE RINGS IN THE MOLECULE

The decomposition of the molecule of a polycyclic compound of this type under electron impact conditions has been examined in greatest detail for hydrocarbons of the steroid and triterpenide types, which is due primarily to their widespread occurrence in nature and the important role which they play in the solution of many geochemical problems.[150]

1. Tetracyclic Hydrocarbons of the Steroid Type

The extensive experimental data obtained in the mass-spectrometric study of the hydrocarbons (LVIII)–(LXI) with the aid of ^{13}C-labelled and deuteriated analogues made it possible to formulate the main pathway leading to the decomposition of the MI and to determine the mechanism of the formation and the structure of the main fragment ions as well as the type of A/B and C/D junctions between the rings in molecules of compound (LXI).[151–156]

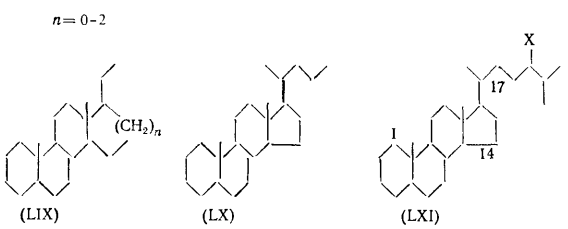


(LVIII)

(LVIIIa): n = 0 (D-norandrostane); (LVIIIb): n = 1 (androstane); (LVIIIc): n = 2 (D-homoandrostane); (LVIIId): n = 3 (D-bishomoandrostane)

The principal pathway in the decomposition of the unsubstituted structure (LVIII) is determined by the structure of the D ring.[41,151,153] The MI peak is intense in the spectra of all the compounds with the exception of compound (LVIIIa). The peak intensity of the ion $[M-CH_3]^+$ in the spectra of compound (LVIII, a, c, and d) is approximately half the maximum value, while in the spectrum of compound (LVIIIb) this is the main peak.

The decomposition of the cyclic component of the molecule of compound (LVIII) takes place with the preferential rupture of the C–C bonds in the A and D rings. Studies of the deuteriated analogues have shown[41,151] that the decomposition of the A ring in compound (LVIIIb) predominates over the decomposition of the D ring, while in compounds (LVIII, a and d) the opposite behaviour obtains. In the case of compounds (LVIII, a, c, and d) this leads to the preferential formation of ions with m/z 217 and 218 [(K) and (L), Scheme 10], while in the case of compound (LVIIIb) ions with m/z 203 and 204 are formed preferentially. The appearance in the D ring of a substituent at the carbon atom adjoining C(13) [pregnanes (LIX), cholanes (LX), and steranes (LXI) have also been investigated][151,156–162] promotes the preferential rupture of the bond between these two atoms, as a result of which the peaks for the ions with m/z 217 and 218 have the maximum intensity in the spectra of compounds (LIX)–(LXI)†.



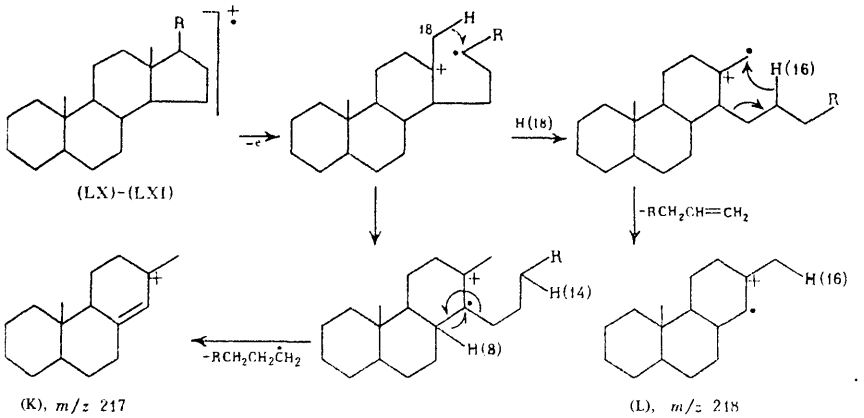
(LIX) (LX) (LXI)

(LVIIIa): (cholestane); (LXIb): X = CH_3 (ergostane); (LXIc): X = C_2H_5 (sitostane)

Attempts to determine structures of this type have been frequently made,[158,159] but only by the analysis of the spectra of deuteriated compounds was it possible to formulate a mechanism of the formation of these ions and to determine their structure (Scheme 10).[151,157]

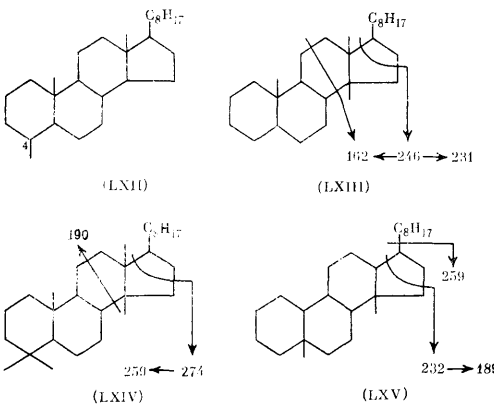
†The presence in the spectra of steranes of intense peaks due to the ions with m/z 217 and 218 makes it possible to determine unambiguously their presence in complex mixtures, which is widely used in the chromato-mass-spectrometric analysis of petroleum fractions.[163–173]

Scheme 10



The ratio of the peak intensities for the ions with m/z 217 and 218 and also the ions with m/z 149 and 151, formed on cleavage of the C ring,[156] plays an important role in the determination of the stereochemical features of molecules of the steranes (LXI, a–c). Thus the first of these characterises the type of C/D junction between the rings (*trans*-junction for $I_{217}/I_{218} > 1$ and *cis*-junction for $I_{217}/I_{218} < 1$), while the second characterises the type of A/B junction between the rings (*cis*-junction for $I_{149}/I_{151} \geq 1$ and *trans*-junction for $I_{149}/I_{151} < 1$).[150]

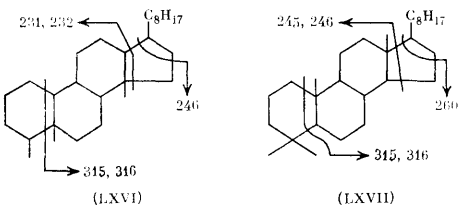
Apart from the hydrocarbons (LVIII)–(LXI) examined above, studies have been made of the spectra of a large group of compounds retaining the skeleton of the molecule of cholestane (LXI), but having methyl groups in other positions in the molecule.



The study of the 4α-methylcholestane (LXII) fragmentation pathway showed[172–174] that the appearance of an additional substituent in the A ring does not alter the principal pathways leading to the decomposition of the molecular ion and characteristic of steranes, merely displacing the mass numbers of the fragment ions incorporating the A ring by 14 a.m.u. towards higher values.

On the other hand, the presence of a substituent at C(14) in 14α-methylcholestane (LXIII) and lanostane (LXIV) [172] alters significantly the MI decomposition pattern. The study of the (LXIII) and (LXIV) fragmentation pathways with the aid of deuteriated analogues showed[175] that the ion with the maximum peak intensity in their spectra [with m/z 231 for (LXIII) and m/z 259 for (LXIV)] is formed from the fragment ions and not from the MI as in the case of cholestane.

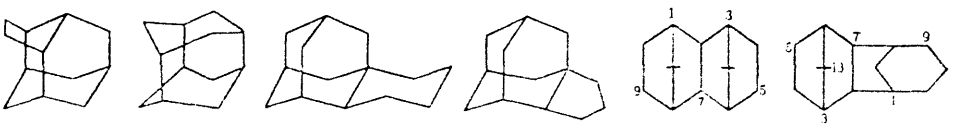
The mass spectra of the stereoisomers of the rearranged cholestane (LXV) are characterised by a high peak intensity of the ions with m/z 189 and 259.[176] The methyl group in the C(5) position in the molecule of compound (LXV) not only shifts by 14 a.m.u. the mass number of the fragments containing the A ring, as in the case of compound (LXII), but also alters sharply the quantitative picture of the spectrum.[174] A characteristic feature of the spectra of the rearranged 4-methylcholestanes (LXVI) is the presence of the intense peaks for the ions with m/z 315 and 316 formed on degradation of the A ring. As for compound (LXV), this is accompanied by the decomposition of the D ring with formation of ions having m/z 232, 231, and 246.



The decomposition of 4,4-dimethylcholestanes (LXVII) under electron impact resembles the decomposition of cholestanes.[175] The mass number of the ions incorporating the A ring is displaced by 28 a.m.u. relative to the corresponding peaks in the spectrum of compound (LXI). Ions which do not incorporate the A ring have the same mass number as for compound (LXIa). For the hydrocarbons (LXV)–(LXVII), there is a possibility, as for cholestane, of the mass-spectrometric determination of the type of A/B and C/D junctions between the rings.[174,176]

2. Other Tetracyclic Hydrocarbons

The molecule of tetracyclo[6.3.1.$0^{2,6}$.$0^{5,10}$]dodecane (LXVIII) can be regarded as the molecule of adamantane having an ethane bridge in the 2,5-positions.



(LXVIII) (LXIX) (LXX) (LXXI) (LXXII) (LXXIII)

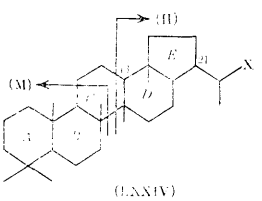
This modification of the adamantane structure does not alter the decomposition of its MI.[177] The MI peak again has the maximum intensity in the spectrum of compound (LXVIII), while the peak of the ion $[M-C_2H_5]^+$ is insignificant. The replacement of the dimethylene bridge by the methylene bridge, as in tetracyclo[5.3.1.$1^{2,6}$.$0^{4,9}$]dodecane, is also hardly reflected in the character of the fragmentation of the MI and the spectrum of compound (LXIX) retains the features characteristic of that of adamantane.[178]

The MI peak intensity remains a maximum also in the spectra of the hydrocarbons (LXX) and (LXXI).[179] However, the stability of the parent ion is greatly reduced compared with its stability in the adamantane spectrum.

The decomposition of the molecules of tetracyclo[6.2.1.$0^{2,7}$.$1^{3,6}$]-dodecane (LXXII) and tetracyclo[6.3.1.$0^{2,7}$.$1^{3,6}$]tridecane (LXXIII) proceeds with formation of the ionic species M^+, $[M-C_2H_4]^+$, $[M-C_2H_5]^+$, and $[M-C_3H_7]^+$, which correspond to intense peaks.[180] The peaks of the secondary ions [*m/z* 80, 121 for (LXXII) and *m/z* 41 for (LXXIII)] have the maximum intensity in the spectra of compounds (LXXII) and (LXXIII).

3. Pentacyclic Hydrocarbons of the Triterpane Series

The study of the fragmentation of hydrocarbons of the triterpane series (LXXIV) (the hopane series) under electron impact showed[172,181,182] that it proceeds with the preferential formation of ions of two types—(M) and (H).

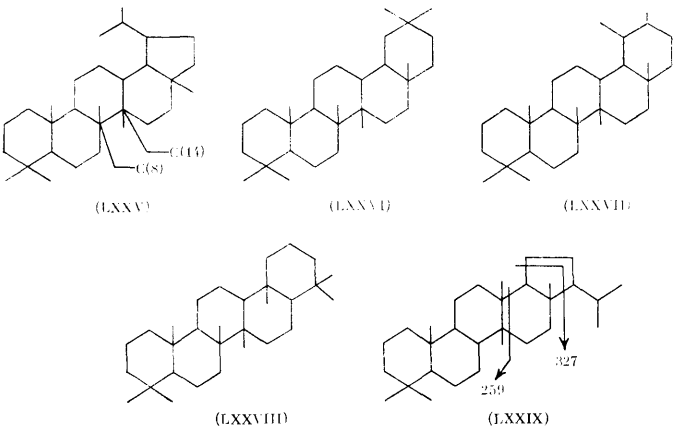


(LXXIV)

(LXXIVa): X = H (adiantane); (LXXIVb): X = CH_3 (hopane); (LXXOVc): X = C_2H_5 (homohopane)

In the case of hopane these ions have equal masses (*m/z* 191). The presence in the spectra of pentacyclic hydrocarbons of the peaks due to the ions (M) and (H), whose intensity greatly exceeds that of the remaining peaks in the spectrum {the peaks of the ions M^+ and $[M-CH_3]^+$ have as a rule low intensities}, has been widely used for the identification of compounds of the "hopane series" in petroleum.[152,183-193] On the other hand, the ratio of the intensities of these peaks is diagnostic for the type of *D/E* ring junction—$I_{(M)}/I_{(H)} > 1$ for the *trans*-junction and $I_{(M)}/I_{(H)} < 1$ for the *cis*-junction.

A change in the position of the substituent in the *E* ring of the hopane molecule does not entail any changes in the spectrum of compound (LXXV).[181,183,184]



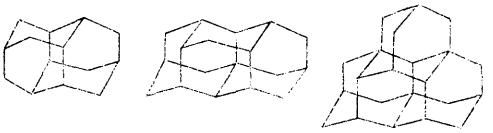
(LXXV) (LXXVI) (LXXVII) (LXXVIII) (LXXIX)

The rupture of the C(8)–C(14) bond is the main process also for compounds with a six-membered *E* ring [oleanane (LXXVI), ursane (LXXVII), and gammacerane (LXXVIII)][181,185] which retain the methyl groups C(8) and C(14).

The transfer of the methyl group from the C(8) position to the C(13) position in structures of type (LXXIX) leads to a sharp decrease of the peak intensity for the ion with *m/z* 191.[172,181] Intense peaks due to the ions with *m/z* 259 and 327, which are absent from the spectra of compounds (LXXIV)–(LXXIX), then appear and there is also a sharp increase of the intensity of the peaks in the region of low masses, which in fact attain maximum values (*m/z* 69, 81, 109).

4. Other Hydrocarbons with Five and More Rings in the Molecule

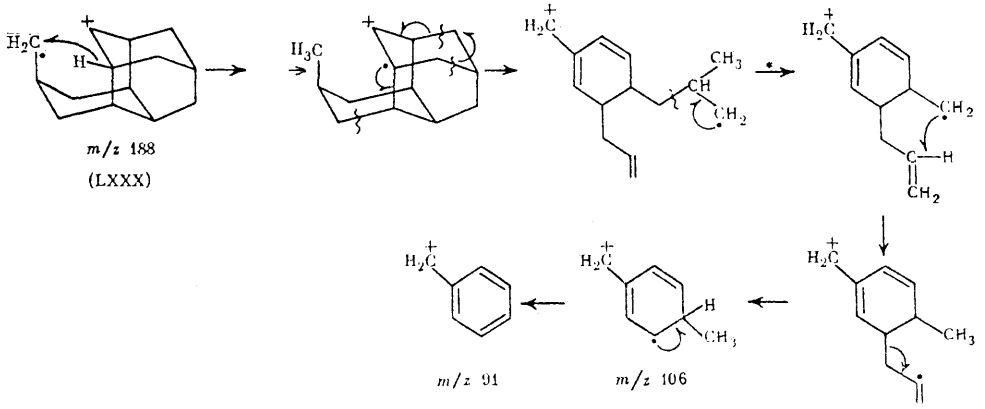
Polycyclic hydrocarbons having adamantane-like structures (LXXX)–(LXXXII) have been studied in detail. As in the spectrum of adamantane, the maximum intensity in their spectra is that of the molecular ion.[193-200]



(LXXX) (LXXXI) (LXXXII)

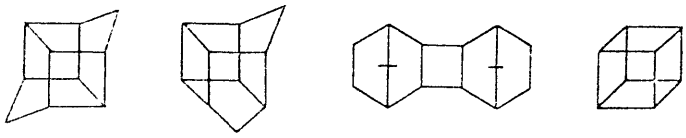
In the diamantane (LXXX) spectrum the intensity of the MI peak is a maximum, being approximately five times greater than that of any other peak.[194,195] The study of the metastable ion peaks in the spectrum of compound (LXXX) showed[196] that the ion with *m/z* 91 which has the next largest peak is not primary, but is formed as a result of a multistage decomposition of the MI and apparently has the structure of the phenylalkyl cation (Scheme 11).

Scheme 11



The spectra of 1-, 3-, and 4-methyldiamantanes retain the type of behaviour in the decomposition of the MI described previously for alkyladamantanes.[197,198] The ratio $I_{[M]^+}/_{[M-CH_3]^+}$ can also be used in this instance for the determination of the position of the methyl group in the diamantane nucleus: it is greater for 3-methyldiamantane than for the 1- and 4-methyldiamantanes.

The decomposition of the MI into two symmetrical fragments with dissociation of the bonds in the cyclobutane rings is characteristic of two pentacyclic hydrocarbons—pentacyclo-[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (LXXXIII) and pentacyclo-[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{5,8}$]decane (LXXXIV).[201] The ion with the cyclopentadiene structure (m/z 66) formed under these conditions exhibits the maximum intensity for both compounds, which is much higher than for the remaining peaks in the spectrum (more than 50% of the total ionic current).



(LXXXIII) (LXXXIV) (LXXXV) (LXXXVI)

The possibility of the symmetric cleavage of the molecule into two fragments of equal mass (with m/z 91) has also been discussed in connection with the dissociation of pentacyclo-[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradecane (LXXXV).[202] However, consideration of the metastable transitions and the spectra of deuteriated analogues showed that the ion $C_7H_7^+$ with m/z 91 is formed as a result of the successive ejection also of C_2 and C_5 fragments from the MI.[202] The ion does not then retain the norbornane structure, but isomerises to a tropylium ion.

The spectrum of "cubane" (LXXXVI), a hexacyclic hydrocarbon with four carbon atoms in the rings, proved to be interesting.[203] The peak for the ion $(M-H)^+$ shows the maximum intensity (this had been observed earlier only in the spectrum of spiropentane[121]).

Mass-spectrometric study of linked-ring adamantane derivatives, containing two adamantyl groups, namely biadamantyls (R–Ad–Ad–R) and diadamantylethanes (Ad–CH_2–CH_2–Ad), showed[204] that the dissociation of the bond between the adamantyl residue Ad and the carbon chain is accompanied by the formation of the radical-ion $[M-AdH]^+$ having an intense peak is characteristic of diamantylethanes, while in the case of biadamantyls the most intense peak in the spectrum corresponds to the rupture of the bond between the adamantyl residues {the $[RAd]^+$ ion}. The above differences persist also for the alkyl derivatives of these structures.

In conclusion one must note yet again that the characteristic features of the decomposition of saturated hydrocarbons under electron impact, mentioned in the present review, necessitate much caution in the approach to the interpretation of the mass spectra and the identification of compounds of this class on that basis. The data available to us do not allow unambiguous conclusions concerning individual structural elements of the molecule, such as the presence (or absence) of a substituent, of a quaternary or tertiary carbon atom, and of bridge type, condensed, or single bond type of connection between the rings in the molecule of the polycyclic hydrocarbon. The solution of these problems is so far possible only in some cases and within the limits of groups of compounds which have been studied systematically.

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Institute of Geology and Development
of Mineral Fuels, Moscow

Translated from *Uspekhi Khimii*, 53, 1523-1547 (1984) U.D.C. 547.421-128.4

Alkoxycarbenium Ions

D.L.Rakhmankulov, R.T.Akhmatdinov, and E.A.Kantor

The method of synthesis, NMR spectra, and chemical properties of alkoxycarbenium ions are examined and the influence of the medium, temperature, and the structure of the ions on their stability are discussed.
The bibliography includes 99 references.

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I. INTRODUCTION

Alkoxycarbenium ions are intermediate in the reactions of organic compounds of many classes: acetals, α-halogenoethers, vinyl ethers, unsaturated ketones, etc. In many respects they determine the reactivity of these compounds and the mode of their reactions. The interest in these compounds is therefore entirely legitimate; since the 1960s, a considerable number of original communications, reflecting particular aspects of the chemistry of alkoxycarbenium ions, have appeared in the literature. Particularly marked progress in this field has been achieved in connection with the development of NMR spectroscopy and the practical applications of the results of research into superacids, which permit the generation of various cations, including alkoxycarbenium ions, and the investigation of their properties under "long life" conditions.

The majority of the reviews and monographs[1-5] devoted to the chemistry of oxonium and in particular alkoxycarbenium ions were published more than ten years ago and reflect inadequately the present advances in this field. In addition, the reviews hardly describe the work of Soviet investigators.

The present review deals with the methods of synthesis of alkoxycarbenium ions, their structure and chemical properties, and the mode of their reactions as a function of the structure of the ions, the reaction conditions, and the character of the nucleophile.

II. METHODS OF SYNTHESIS OF ALKOXYCARBENIUM IONS

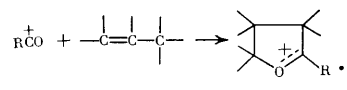
The methods of synthesis of alkoxycarbenium ions are fairly varied. In terms of the principles underlying the synthesis, the methods can be divided into seven groups:

1. Alkylation of the carbonyl group:

$$\rangle C{=}O + R^+ \rightarrow \rangle C^{+}\!\cdots\!OR \ .$$

Cyclic alkoxycarbenium ions are mainly obtained by this procedure as a result of the intramolecular alkylation of the carbonyl groups of aldehydes and ketones containing other functional groups.

2. Acylation of olefins and cyclopropanes:



3. Protonation of vinyl ethers:

$$-\overset{|}{C}{=}\overset{|}{C}-OR + H^+ \rightarrow -\overset{|}{C}H-\overset{|}{C}^{+}\!\cdots\!OR \ .$$

4. Abstraction of the halide anion from α-halogenoethers:

$$R_2C(X)-OR' \xrightarrow{-X^-} R_2C^{+}\!\cdots\!OR' ;$$
X=Cl, Br, I.

5. Abstraction of the alkoxy-group from acetals by protic or aprotic acids:

$$ROCOR \xrightarrow{+H^+} ROC^{+}OR \xrightarrow{-ROH} -\overset{|}{C}^{+}\!\cdots\!OR \ .$$
H

6. The formation of the carbenium centre at a site in the molecule remote from the oxygen atom with subsequent hydride or alkyl shift:

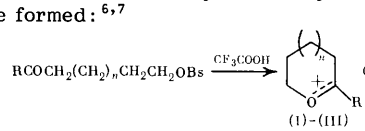
$$-\overset{+}{C}-\left(-\overset{|}{C}-\right)_n-\overset{|}{C}R-OR' \longrightarrow -\overset{|}{C}R-\left(-\overset{|}{C}-\right)_n-\overset{|}{C}^{+}\!\cdots\!OR' ;$$
n=0, 1; R=H, Alk.

7. Isomerisation of oxenium ions:

$$-\overset{|}{C}R-\overset{+}{O} \longrightarrow -\overset{|}{C}^{+}\!\cdots\!OR \ .$$

1. Alkylation of the Carbonyl Group

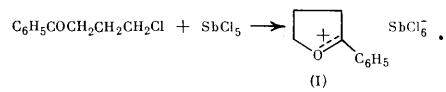
The intramolecular alkylation methods differ in the procedure used to generate the alkyl cation attacking the carbonyl group. The solvolysis of brosylates or the elmination of a halogen are the most convenient for the generation of primary alkyl cations. Thus, when the brosylates of γ- and δ-hydroxyketones are dissolved in trifluoroacetic or formic acid, five- and six-membered cyclic alkoxycarbenium ions (I)–(III) are formed:[6,7]



(I)-(III)

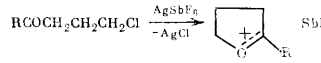
(I) $n=0$, $R=C_6H_5$; (II) $n=0$, $R=CH_3$;
(III) $n=1$, $R=C_6H_5$; OBs = p-$BrC_6H_4SO_2O$.

Unambiguous evidence supporting the formation of the ion (I) is provided by the identity of the ^1H NMR spectrum with that of a solution of the salt obtained by treating γ-chlorobutyrophenone with antimony pentachloride in SO_2 or acetonitrile:[7]

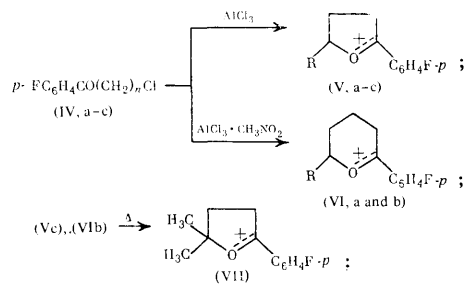


(I)

The chloride ion can also be removed by treatment with silver salts:[8]



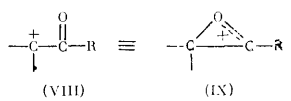
Analogous ions are formed on interaction of ω-chlorophenones (IV, a–c) with aluminium chloride.[9,10] It is of interest that, on treatment with free $AlCl_3$, only the five-membered cyclic ion (Vb) is formed from the ketone (IVb), while on treatment with the complex $AlCl_3.CH_3NO_2$, a mixture of five-membered (V, b and c) and six-membered (VI, a and b) cyclic alkoxycarbonium ions is formed with the five-membered ions predominating. On heating, the ions (Vc) and (VIb) are converted into the more stable ion (VII):



(IV): $n = 3$ (a), 4 (b), 5 (c); (V), (VI): R = H (a), CH_3 (b), C_2H_5 (c).

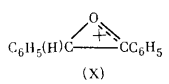
Thus five-membered cyclic alkoxycarbenium ions are more stable than the six-membered ions.

Three- and four-membered cyclic alkoxycarbenium ions are apparently unstable. It has been suggested[11] that α-acylcarbenium ions can have the cyclic structure as a result of the interaction of a vacant orbital with the unshared electron pairs of the carbonyl oxygen atom:



(VIII) (IX)

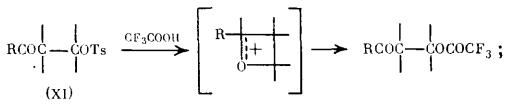
Quantum-chemical calculations have shown[12] that structure (IX) should be more stable than structure (VIII). At −75 °C signals due to the first representative of three-membered cyclic alkoxycarbenium ions (X) were detected in ^1H and ^{13}C NMR spectra:[12]



(X)

α-Acylcarbenium ions have been in many instances suggested as intermediates.[8,11–17]

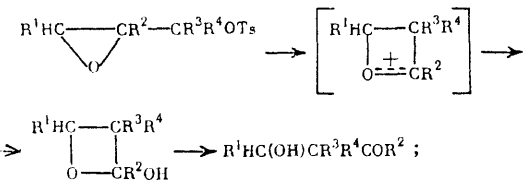
The formation of four-membered cyclic alkoxycarbenium ions has been postulated in a number of studies.[18–21] In particular, their formation is indicated by the results of the solvolysis of compounds of type (XI) in trifluoroacetic acid:[18,19]



(XI)

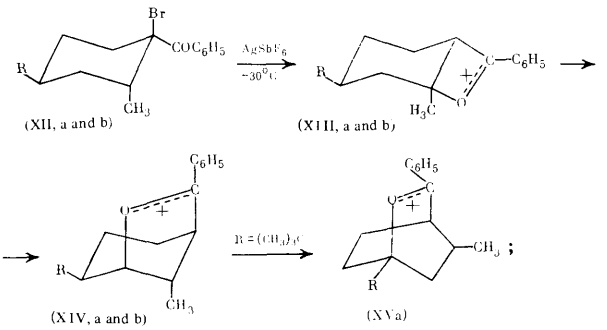
R = p-$CH_3OC_6H_4$, p-$NO_2C_6H_4$, C_6H_5, CH_3.

The study of the kinetics and stereochemistry of the products of the solvolysis of oxiranylmethyl toluene-*p*-sulphonates also led to the conclusion that such ions are formed:[20]



$R^1 - R^4$ = H, CH_3.

Four-membered cyclic alkoxycarbenium ions were first detected by NMR after the elimination of the bromide anion from α-bromoketones.[12,13] The ions (XIII, a and b) were detected following the interaction of the ketones (XII, a and b) with $AgSbF_6$ at −30 °C:

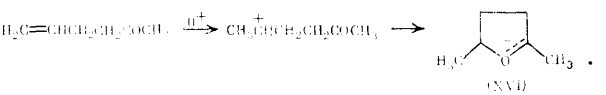


(XII)–(XV): R = $(CH_3)_3C$ (a), H (b).

When the temperature is raised to 25 °C, the ions (XIII, a and b) isomerise to the more stable five-membered ions (XIV, a and b), and t-butyl-substituted ions (XIVa) can isomerise in their turn to the six-membered ions (XVa).

When the reaction is carried out at room temperature, five- and six-membered cyclic alkoxycarbenium ions are formed immediately.[14–16]

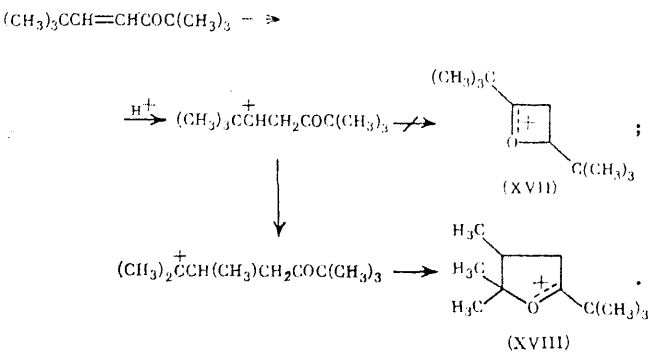
The most convenient method of synthesis of cyclic alkoxycarbenium ions involves the protonation of unsaturated ketones. When the protonation leads to the formation of a carbenium centre in the γ- or δ-position relative to the carbonyl group, the cations cyclise and give rise to five- and six-membered cyclic ions respectively,[22–32] for example:



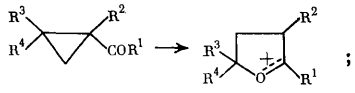
(XVII)

The cyclisation takes place under the influence of both various superacids[22,27–30] and also weaker acids such as HBF_4,[31] $HClO_4$,[32] concentrated sulphuric acid,[23,24] and dilute sulphuric acid.[25] This method of synthesis has been used to determine the heats of formation of alkoxycarbenium ions.[23,24]

If the protonation leads to the formation of a carbenium centre in the β-position relative to the carbonyl group, the corresponding four-membered alkoxycarbenium ions (XVII) are not formed and instead a rearrangement takes place (provided that it is feasible), which leads to the formation of five-membered cyclic alkoxycarbenium ions (XVIII).[31–33]

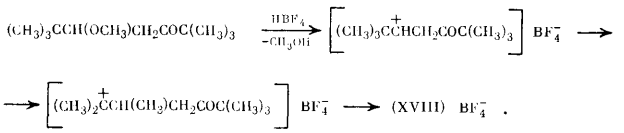


Cyclic alkoxycarbenium ions are also formed on protonation of cyclopropryl ketones in 75–96% H_2SO_4:[34,35]

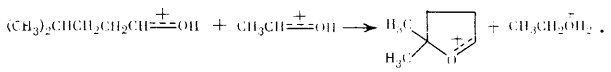


R^1–R^4 = H, CH_3, C_6H_5, cyclo-C_3H_5.

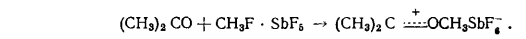
In some cases the abstraction of the alkoxy-group by strong acids has been used to generate the alkyl cation alkylating the carbonyl group:[31]



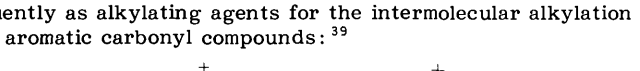
The carbenium centre attacking the carbonyl group can be created also by abstracting a hydride ion from the γ- and δ-positions relative to the carbonyl group. Thus, when 4-methylvaleraldehyde reacts with acetaldehyde in the 9 : 1 HF–SbF_5 system, the protonated acetaldehyde acts as the acceptor of the hydride ion. The dication formed from the protonated 4-methylvaleraldehyde abstracts a proton from the oxygen atom and is converted into a cyclic ion:[36]

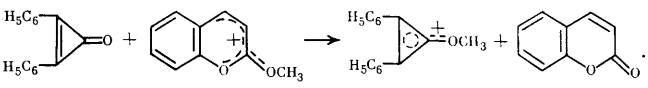


The ethanol formed is protoned in this medium. Only aromatic carbonyl compound readily undergo intermolecular alkylation. The majority of aliphatic aldehydes and ketones undergo the aldol condensation under alkylation conditions,[1,37] but, on treatment with $CH_3F.SbF_5$ in SO_2 at −78 °C, it is possible to methylate also aliphatic ketones:[38]



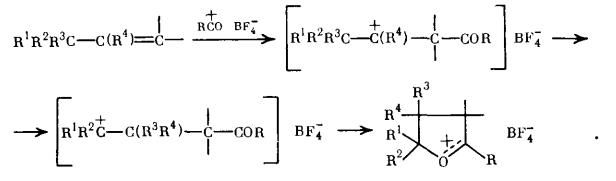
Trialkyloxonium or dialkoxycarbenium ions are used frequently as alkylating agents for the intermolecular alkylation of aromatic carbonyl compounds:[39]



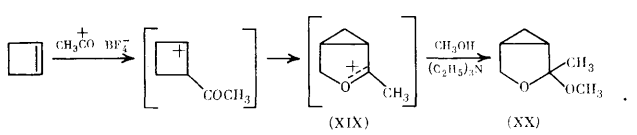


2. Acylation of Olefins and Cyclopropanes

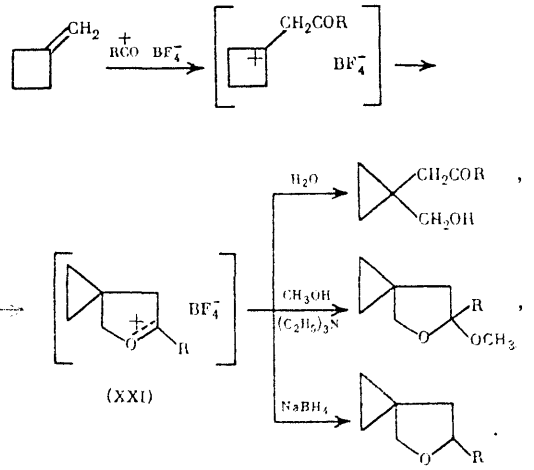
A novel method for the simultaneous introduction of the carbonyl group and the generation of the carbonium ion leading to the formation of cyclic alkoxycarbenium ions involves the acylation of olefins:[40–46]



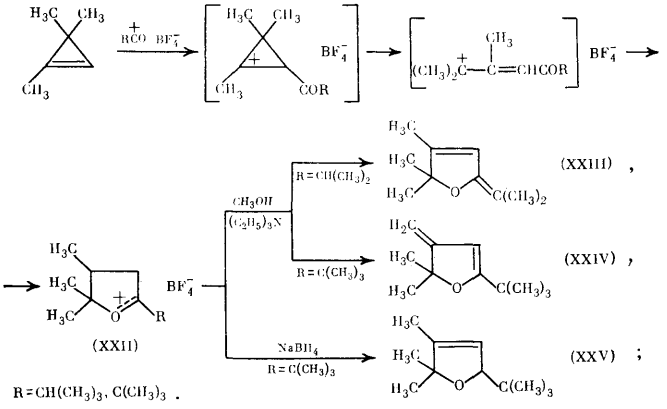
Both acylic and cyclic olefins enter into this reaction.[40–42] After the addition of the acyl cation, a 1,2-hydride or 1,2-alkyl shift and cyclisation take place. In the acylation of cyclobutene the ring contracts and the bicyclic cation (XIX) is formed.[43] Its treatment with a methanol solution of triethylamine leads to the formation of the acetal (XX):



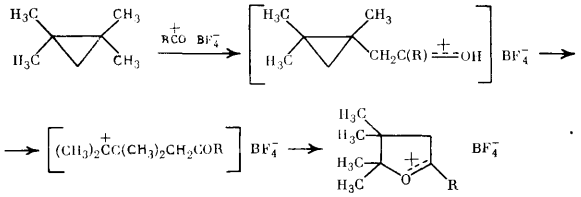
In the acylation of methylenecyclobutane cyclic alkoxycarbenium ions are formed only when pivaloyl and isobutyryl tetrafluoroborates are used.[44,45] Ring contraction also takes place in this instance. The formation of the alkoxycarbenium ion (XXI) has been confirmed by its subsequent reactions:



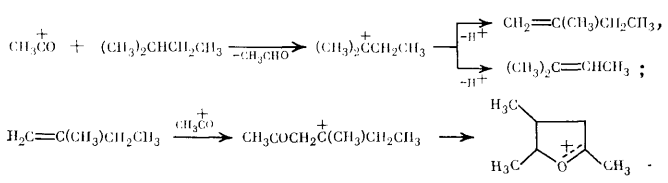
Alkoxycarbenium ions (XXII) of the dihydrofuran series are formed on acylation of 1,3,3-trimethylcyclopropene with pivaloyl or isobutyryl tetrafluoroborate:[46]



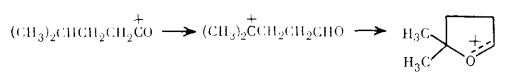
Analogous results have been obtained also on acylation of cyclopropanes.[47] The reaction of acyl cations with 1,1,2,2-tetramethylcyclopropane is somewhat unusual. Using tracer atoms, it has been shown that the ring is not attacked directly by the acyl cation; the authors proposed the following reaction mechanism:[47]



Cyclic alkoxycarbenium ions can be obtained by the reaction of acylcations with alkanes containing a tertiary carbon atom. The acyl cation then abstracts a hydride ion and is reduced to an aldehyde. The tertiary alkyl cation formed is converted into an olefin, which reacts with yet another acyl cation to form an alkoxycarbenium ion:[48]

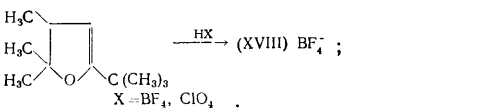


An example of an intramolecular reaction of this kind is provided by the isomerisation of acyl cations to alkoxycarbenium ions in superacid media:[36,49]

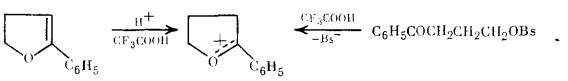


3. Protonation of Vinyl Ethers

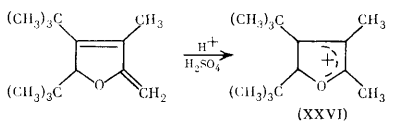
Alkoxycarbenium ions can be obtained by protonating vinyl ethers. Thus, when 2-t-butyl-4,5,5-trimethyl-4,5-dihydrofuran is mixed in the cold with an ethereal solution of HBF_4[31] or with $HClO_4$,[32] the salt of the corresponding cation (XVIII) is formed:



The addition of a proton on dissolution of 2-phenyl-4,5-dihydrofuran in trifluoroacetic acid has been used to identify the ion (I) formed on solvolysis of γ-hydroxybutyrophenone brosylate in trifluoroacetic acid:[6,7]

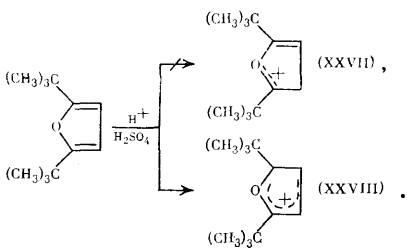


When 4,5-di-t-butyl-3-methyl-2-methylene-2,5-dihydrofuran is dissolved in sulphuric acid, the ion (XXVI), where the positive charge is distributed over four atoms, is formed:[50]



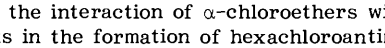
(XXVI)

It is remarkable that only the more stable ion (XXVIII) is formed when 2,5-di-t-butylforan, whose protonation can result in the formation of the two ions (XXVII) and (XXVIII):[50]

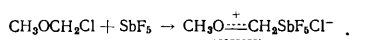


4. Abstraction of a Halide Anion from α-Halogenoethers

α-Halogenoalkyl ethers are themselves incapable of ionising with elimination of a halide anion. The ionisation is promoted by the binding of the halide, for example, in a complex anion on treatment with certain metal polyhalides. Antimony pentachloride or pentafluoride is most frequently used for this purpose. Thus the interaction of α-chloroethers with $SbCl_5$ at −75 °C results in the formation of hexachloroantimonates of the corresponding cations:[51]

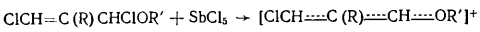


When α-halogenoethers are treated with a solution of SbF_5 in SO_2, the alkoxycarbenium ions formed remain in solution, which makes it possible to investigate them by NMR:[52–54]

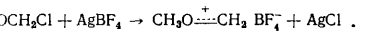


(XXIX)

Alkoxycarbenium ions are formed particularly readily from α-halogenoallyl ethers:[55]

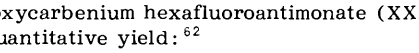


A convenient method for the synthesis of alkoxycarbenium ions from α-halogenoethers involves treatment of the latter with silver salts such as $AgSbF_6$, $AgBF_4$, or $AgOSO_2C_6H_2(NO_2)_3$,[56–61] for example:



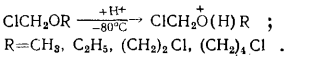
(XXIX)

The halide anions can also be bound by protonation on treatment with strong acids. For example, when chloromethyl methyl ether is treated with a mixture of HF and SbF_5, methoxycarbenium hexafluoroantimonate (XXIX) is formed in quantitative yield:[62]

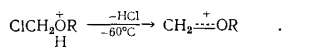


(XXIX)

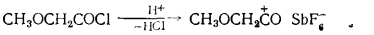
Interesting results have been obtained in the study of this reaction by ^1H NMR in the HSO_3F–SbF_5–SO_2 system at low temperatures.[63] When α-halogenoethers are dissolved in this mixture at −80 °C, the oxygen atom is protonated with the consequent formation of oxonium ions:



On raising the temperature to −60 °C, the oxonium ions slowly split off HCl and are converted into alkoxycarbenium ions:

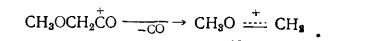


The formation of alkoxycarbenium ions from alkoxyacetic acid chlorides can also be regarded as an application of this method. When methoxyacetic acid chloride is dissolved in the HF–SbF_5 mixture at −60 °C, the oxocarbenium ion (XXX) is formed:[62]



(XXX)

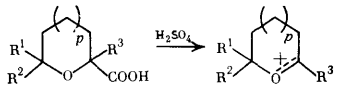
On raising the temperature, the ion (XXX) slowly splits off a molcule of carbon monoxide and is converted into the methoxycarbenium ions (XXIX):



(XXIX)

Decarboxylation of carboxylic α-alkoxyacids also constitutes a procedure closely resembling the above method. Thus, when tetrahydrofuran- and tetrahydropyran-2-carboxylic acids are

dissolved in 96% H_2SO_4, the carboxy-group is split off and five- and six-membered cyclic alkoxycarbenium ions are formed respectively:[64]



$R^1-R^3 = H, CH_3$; $p = 0.1$.

The six-membered ions are in equilibrium with the isomeric five-membered ions.

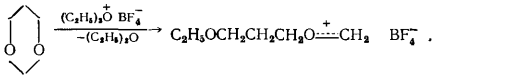
5. The Synthesis of Alkoxycarbenium Ions from Acetals

Like α-chloroethers, acetals are extremely convenient precursors for the generation of alkoxycarbenium ions. The alkoxy-group is a much more powerful nucleophile than the halide anion and its elimination from the acetal molecule therefore requires preliminary electrophilic attack on the oxygen atom.

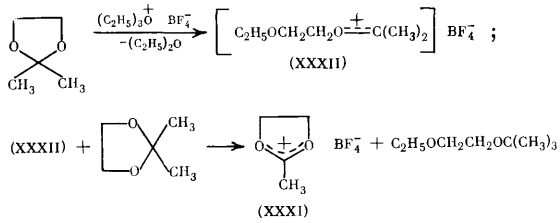
One of the first method described in the literature for the preparation of alkoxycarbenium ions and acetals involves treatment of the latter by trialkyloxonium salts:[65]

$$(CH_3)_3CC(CH_3)(OCH_3)_2 \xrightarrow[-2(CH_3)_2O]{(CH_3)_2\overset{+}{O}BF_4^-} (CH_3)_3CC(CH_3)\overset{+}{=}OCH_3BF_4^- .$$

Under the influence of trialkyloxonium salts, the ring in cyclic acetals is cleaved, which entails the formation of alkoxycarbenium ions:[66-68]



When cyclic ketals are treated with trialkyloxonium salts, cyclic dioxolenium ions (XXXI) are formed. It has been suggested[69] that acyclic alkoxycarbenium ions (XXXII) are formed initially and then abstract an alkyl anion from a second ketal molecule, for example:



(XXXII)

(XXXI)

The same reactions take place when cyclic ketals are treated with other electrophiles, such as dialkoxycarbenium ions, Lewis acids, and RHal–$AgBF_4$ mixtures.[69]

BF_3 or $SbCl_5$ are most often used as the Lewis acids.[70] Thus, when BF_3 interacts with benzaldehyde dimethyl acetal, salts (tetrafluoroborates) are formed. The mechanism of their formation can be described schematically as follows:[70]

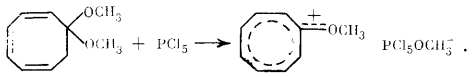
$$C_6H_5CH(OCH_3)_2 + BF_3 \rightarrow \underset{\text{(XXXIII)}}{C_6H_5CH\overset{+}{=}OCH_3} \quad BF_3OCH_3^- ;$$

$$3BF_3OCH_3^- + BF_3 \rightarrow 3BF_4^- + B(OCH_3)_3 .$$

The anion $BF_3OCH_3^-$ formed initially is unstable and its interaction with the excess BF_3 converts it into the stable anion BF_4^-, which reacts with the cation (XXXIII) to form the salt $C_6H_5\overset{+}{C}H{-}OCH_3BF_4^-$, which is insoluble in the reaction mixture.

It is noteworthy that, when this reaction is carried out in $CDCl_3$ as the solvent, the anion $BF_3OCH_3^-$ does not disproportionate and the salt remains in solution, which makes it possible to investigate this reaction by ^1H NMR.[71,72] The introduction of electron-accepting groups in the *para*-position in the benzene ring reduces the reactivity of the acetal and *p*-nitrobenzaldehyde dimethyl acetal does not react with BF_3 at all.[72]

Weaker Lewis acids have also been used to obtain more stable alkoxycarbenium ions. Thus treatment of a solution of 7,7-dimethoxycyclo-octa-1,3,5-triene in liquid SO_2 with PCl_5 or $SOCl_2$ at −20 °C results in the formation of the 1-methoxycyclo-octatrienylium ion:[73]



Molecular bromine can also be used as the electrophile for the abstraction of the alkoxy-group.[74,75] When 2,2-dimethoxypropane reacts with bromine in SO_2 at −60 °C, the methoxydimethylcarbenium ion (XXXIV) is formed:

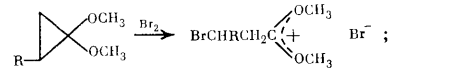
$$(CH_3)_2C(OCH_3)_2 + Br_2 \rightarrow \underset{\text{(XXXIV)}}{(CH_3)_2C\overset{+}{=}OCH_3}\ Br^- + CH_3OBr .$$

Benzaldehyde, acetophenone, benzophenone, cyclohexanone, cycloheptanone, and cyclobutanone dimethyl acetals behave analogously.[75]

The ions formed from acetaldehyde and formaldehyde acetals are unstable under these conditions and, having combined with the Br^- counterion, are converted into the corresponding α-bromoethers:

$$RCH(OCH_3)_2 \xrightarrow[-CH_3OBr]{Br_2} [RCH\overset{+}{=}OCH_3]Br^- \rightarrow RCHBrOCH_3 ;$$
$$R = H,\ CH_3 .$$

In cyclopropanone dimethyl acetals, the cyclopropane ring is more reactive in relation to bromine, which leads to the formation of β-bromoethyldimethoxycarbenium ions:[75]



$R = H, C_6H_5$.

The simplest method of synthesis of alkoxycarbenium ions from acetals involves treatment of the latter with strong acids. This method is also convenient because in this instance the ions are in solution and can be investigated by ^1H NMR. Depending on the stability of the alkoxycarbenium ions, acids of different strengths must be used for their generation. For example, the simplest alkoxycarbenium ion, namely the methoxycarbenium ion, has been obtained in an acid as strong as the equimolar mixture of HSO_3F and SbF_5 diluted with liquid SO_2 to reduce its viscosity:[54]

$$CH_2(OCH_3)_2 \xrightarrow[HSO_3F-SbF_5]{2H^+} \underset{\text{(XXIX)}}{CH_2\overset{+}{=}OCH_3} + CH_3\overset{+}{O}H_2 .$$

The methanol split off is protonated in this medium. At −60 °C there is almost no proton exchange with the medium. The splitting of the signal due to the methyl group of the protonated methanol into a triplet is observed in ^1H NMR spectrum (as a consequence of the spin–spin coupling with the protons of the $\overset{+}{O}H_2$ groups), which permits an unambiguous assignment of the signals of the methyl groups of methanol and methoxycarbenium.

The presence of substituents at the acetal carbon atom increases the stability of the ions formed from the acetals and they become stable in less acid media. Thus the methoxydimethylcarbenium ion (XXXIV) can be obtained at room temperature in 30% oleum:[76]

$$(CH_3)_2C(OCH_3)_2 \xrightarrow[H_2SO_4-SO_3]{H^+} \underset{\text{(XXXIV)}}{(CH_3)_2C\overset{+}{=}OCH_3} + CH_3OH .$$

The alkoxycarbenium ions derived from ketone and benzaldehyde acetals at −60 °C can be obtained even on treatment with HBr:[74]

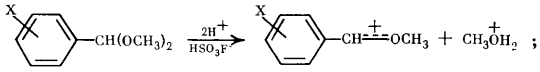
$$RR^1C(OCH_3)_2 \xrightarrow[-60°C]{HBr} RR^1C^{+}{-}OCH_3 + CH_3\overset{+}{O}H_2 ;$$
$$R=R^1=CH_3;\quad R=R^1=C_6H_5;\quad R=H,\ R^1=C_6H_5;\quad R=CH_3,\ R^1=C_6H_5 .$$

Under these conditions, the methanol is also present in the protonated form.

HSO_3F is most often employed to obtain alkoxycarbenium ions from acetals. The possibility of the generation and the stability of alkoxycarbenium ions in HSO_3F depend on the structure of the acetal and temperature. The dissolution of ketals even at room temperature leads to the formation of alkoxycarbenium ions:[77]

$$C_6H_5C(CH_3)(OCH_3)_2 \xrightarrow[HSO_3F]{2H^+} C_6H_5C(CH_3)\overset{+}{-}OCH_3 + CH_3\overset{+}{O}H_2 .$$

As in the $HSO_3F-SbF_5-SO_2$ mixture, methanol is present in the protonated form, as shown by the identity of the chemical shifts of the signals of the methyl protons in the two media. However, owing to the rapid proton exchange with the medium, there is no splitting of the signal into a triplet. The protonated methanol is therefore a convenient internal standard. The dimethyl acetals of substituted benzaldehydes give rise to alkoxycarbenium ions on dissolution in HSO_3F at −60 °C:[71,72,78]



X = H, 4-CH_3, 4-OCH_3, 4-Cl, 4-Br, 4-F, 3-F, 2-CH_3, 2-OCH_3, 4-NO_2 .

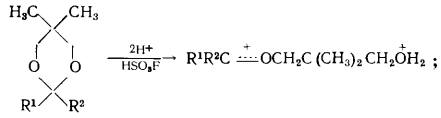
It was noted above that the corresponding ion cannot be obtained from the dimethyl acetal of *p*-nitrobenzaldehyde on treatment with BF_3. In HSO_3F this ion is formed readily.

Furthermore, the corresponding dications $CH_3O\overset{+}{-}CHC_6H_4.\overset{+}{C}H{-}OCH_3$ have been obtained from the bis(dimethyl acetals) of *o*-, *m*-, and *p*-phthaladehydes.[72,78] All the ions obtained are stable when the temperature is raised to 36 °C. The dissolution of the acetals of aliphatic aldehydes in HSO_3F at −70 °C results in the formation of alkoxycarbenium ions, whose stability depends on temperature:[79-81]

$$RCH(OR^1)_2 \xrightarrow[HSO_3F]{2H^+} RCH\overset{+}{-}OR^1 + R^1\overset{+}{O}H_2 ;$$
$$R=H,\ CH_3,\ C_2H_5;\ R^1=CH_3,\ C_2H_5,\ C_3H_7,\ CH(CH_3)_2 .$$

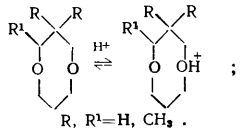
When R = alkyl, the ions are fairly stable at room temperature and appreciable changes in the ^1H NMR spectrum are observed only over a period of 2–3 h. When R = H, the ions are stable in the range between −70° and −30 °C.

The behaviour of cyclic acetals and ketals in HSO_3F does not differ from that of their acyclic analogues. At −70 °C the ring is opened, which entails the formation of the corresponding dications,[82,83] for example:



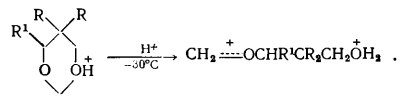
$R^1=R^2=CH_3;\quad R^1=H,\ R^2=C_6H_5 .$

In their response to treatment with HSO_3F, cyclic formals differ from all the acetals described previously. The point is that the formation of alkoxycarbenium ions from acetals is a two-stage process. In the first stage the acetal is protonated with formation of an oxonium ion. The alkoxycarbenium ion is formed after the subsequent elimination of an alcohol molecule from the oxonium ion. However, when the acetals described previously were allowed to react with acids, the intermediate oxonium ions were not detected. Only on dissolution in HSO_3F of certain cyclic formaldehyde acetals at −70 °C was it possible to detect oxonium ions by ^1H NMR:[83,84]



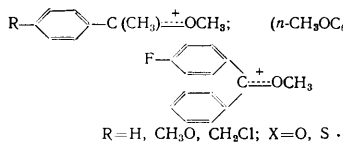
R, R^1=H, CH_3 .

The ^1H NMR spectrum indicates the retention of the ring at temperatures between −70 °C and −40 °C, although the signal of the oxonium proton is not observed as a consequence of the rapid proton exchange.[84] Above −40 °C, ring opening takes place:



However, the alkoxycarbenium ions formed are unstable and rapidly undergo further reactions.[84]

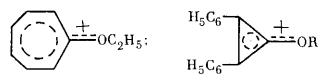
In less acidic media the alkoxycarbenium ions derived from acetals can be obtained and detected only in exceptional cases. Thus in solution in 96–100% H_2SO_4 the following ions derived from the corresponding acetals were detected by ^1H NMR at room temperature:[85]



R = H, CH_3O, CH_2Cl; X = O, S .

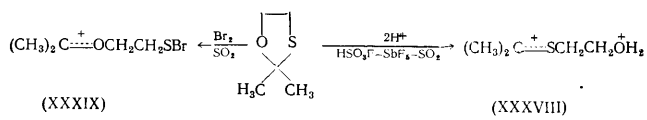
In more dilute H_2SO_4 solutions the formation of alkoxycarbenium ions from acetals cannot be detected by NMR.[85]

The ions (XXXV)–(XXXVII) have been detected by ultraviolet spectroscopy under conditions where the rate of their formation exceeds the rate of their hydrolysis:[86]



(XXXV) (XXXVI): R = CH_3; (XXXVII): R = C_2H_5 .

In the presence of various heteroatoms in the acetal molecule the direction of attack depends on the nature of the attacking reagent. Thus, when 2,2-dimethyloxathiolan is dissolved in the $HSO_3F-SbF_5-SO_2$ mixture at −60 °C, the alkylthiocarbenium ion (XXXVIII) is formed, while the interaction with bromine in SO_2 at −80 °C leads to the alkoxycarbenium ion (XXXIX):[87]



(XXXIX) (XXXVIII)

The authors[87] explained these results by the lower basicity but greater nucleophilicity of the sulphur atom compared with the oxygen atom.

6. Rearrangement of Oxygen-containing Carbenium Ions

When a positive charge is generated in the molecules of ethers on a carbon atom not adjoining the oxygen atom, a rearrangement leading to alkoxycarbenium ions is frequently

observed. For example, when 2-halogeno-3-methoxy-2,3-dimethylbutane is dissolved in the SbF_5-SO_2 or $HSO_3F-SbF_5-SO_2$ mixture at −60 °C, the t-butylmethoxymethylcarbenium ion is produced:[88]

$$(CH_3)_2CXC(CH_3)_2OCH_3 \xrightarrow[-SbF_4X]{SbF_5} [(CH_3)_2\overset{+}{C}C(CH_3)_2OCH_3] \rightarrow (CH_3)_3CC(CH_3)=\overset{+}{O}CH_3;$$
X=Cl, Br, I.

The dissolution of alkoxyalcohols in the $HSO_3F-SbF_5-SO_2$ mixture at −60 °C leads to oxonium dications. On raising the temperature, some of them are dehydrated with formation of alkoxycarbenium ions,[53] for example:

$$CH_3OCH_2CH(CH_3)OH \xrightarrow[-60°C]{2H^+} CH_3\overset{+}{O}(H)CH_2CH(CH_3)\overset{+}{O}H_2 \xrightarrow[-10°C]{-H_2O,\ -H^+} \longrightarrow CH_3O\overset{+}{=}CHCH_2CH_3;$$

$$C_2H_5O(CH_2)_3OH \xrightarrow[-60°C]{2H^+} C_2H_5\overset{+}{O}(H)(CH_2)_3\overset{+}{O}H_2 \xrightarrow[0°C]{-H_2O,\ -H^+} C_2H_5O\overset{+}{=}CHCH_2CH_3.$$

7. Isomerisation of Oxenium Ions

The isomerisation of unstable oxenium ions formed in certain reactions constitutes a fairly unusual method for the formation of alkoxycarbenium ions. Thus, when t-alkyl hydroperoxides are dissolved in superacids, alkoxydialkylcarbenium ions (XXXIV) are formed:[89,90]

$$(CH_3)_3COOH \xrightarrow{H^+} [(CH_3)_3C\overset{+}{O}OH_2] \xrightarrow[-H_2O]{} [(CH_3)_3C-\overset{+}{O}] \rightarrow (CH_3)_2C=\overset{+}{O}CH_3.$$
(XXXIV)

The formation of alkoxycarbenium ions via the isomerisation of intermediate oxenium ions has been observed in the oxidation with ozone in superacids of stable t-alkyl cations,[91] branched hydrocarbons,[92,93] and alcohols,[94] in the oxidation of hydrocarbons in superacids with hydrogen peroxide,[93,95] and on dissolution of t-alkyl esters of peracids in superacids.[96]

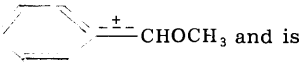
III. THE STRUCTURE AND PROPERTIES OF ALKOXYCARBENIUM IONS

It follows from the analysis of the methods of synthesis of alkoxycarbenium ions presented above that almost all these ions are stable at low temperatures in weakly nucleophilic media such as HSO_3F and $HSO_3F-SbF_5-SO_2$. With increase of temperature and of the nucleophilicity of the medium, the stability of the alkoxycarbenium ions falls. The cyclic ions are more stable than the acyclic ions; many cyclic alkoxycarbenium ions exist at room temperature in H_3SO_4 [23,24] and in trifluoroacetic acid in the absence of trifluoroacetate anions.[6,7]

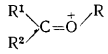
The stability of acyclic alkoxycarbenium ions depends to a large extent on the presence of electron-donating substituents at the carbenium carbon atom. Alkoxycarbenium ions without substituents at the carbenium centre are stable in HSO_3F only at temperatures not exceeding −30 °C, while their methyl-substituted analogues are stable even at room temperature.[44,45,49] Electron-accepting substituents destabilise alkoxycarbenium ions. Thus the methoxy-4-*p*-nitrophenylcarbenium ion is not formed from the corresponding acetal on treatment with BF_3, although the dimethyl acetals of other substituted benzaldehydes are converted into methoxyarylcarbenium ions under the same conditions.[71,72] The use of a less nucleophilic medium (HSO_3F), which tends to increase the stability of the ions, makes it possible to obtain not only the nitrophenyl-substituted cation but also the dications.[72,78]

Protons at the carbenium carbon atom give rise to signals in the ^1H NMR spectra of alkoxycarbenium ions in a very low field (Table 1), which indicates their carbenium character. This is also indicated by the downfield shift of the signals of the α-protons of the substituents at the carbenium centre. The chemical shifts of the benzyl protons in the ^1H NMR spectra of aryl-substituted alkoxycarbenium ions depend on the positions and character of the substituents (Table 2) and are better correlated with the δ^+ constants of the substituents ($\delta_{H_\alpha} = 0.588\delta^+ + 9.078$, $r = 0.972$) [72] than with the σ constants ($r = 0.852$), which is a consequence of the carbenium character of the ions.

The substitution of the chemical shifts for the benzyl protons in the *meta*- and *para*-dications in the correlation expression made it possible to determine the σ^+ constants for the substituent $-CH=\overset{+}{O}CH_3$ ($\sigma_m^+ = 0.916$; $\sigma_p^+ = 1.074$).[72] It follows from these values that the $-CH=\overset{+}{O}CH_3$ group is a stronger electron acceptor than the nitro-group.

The carbenium centre is conjugated with the aromatic ring, which hinders rotation about the partially double bond  and is manifested by some non-equivalence of the protons in the aromatic ring in the *para*-substituted ions.[71]

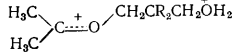
On the other hand, alkoxycarbenium ions also have some oxonium character, which is indicated, for example, by the correlation between the chemical shift of the protons of the methoxy-groups and the σ^+ constants of the substituents in aryl-substituted alkoxycarbenium ions.[72] In the oxonium form of the ions the bond between the oxygen and the carbon should be double:



This leads to the non-equivalence of the substituents R^1 and R^2 (when $R^1 = R^2$) and the existence of two isomers of the ions for $R^1 \neq R^2$. The chemical shifts of the methylene protons in the ^1H NMR spectrum of the methoxycarbenium ion (XXIX) at −60 °C differ by 0.12 p.p.m. In addition, these protons interact with one another, the corresponding constant being $J = 20.79$ Hz, and with the protons of the methoxy-group, the corresponding constants being $J = 0.83$ and 0.97 Hz. An analogous fact has been established also for the chloromethoxycarbenium ion (XL) (Table 1).[54]

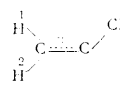
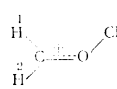
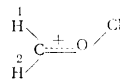
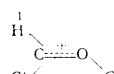
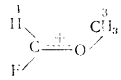
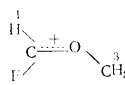
Recent analysis of the ^{17}O NMR spectra showed that the degree of π-bonding in the methoxydimethylcarbenium ion (XXXIV) is ~60%.[38]

The partially double bond is retained even at room temperature. Thus the chemical shifts of the signals of the methyl groups at the carbenium centre in the ^{13}C NMR spectrum of the ion (XLIa) are different at −60 °C (32.6 and 27.8 p.p.m.),[94] while for the analogous ion (XLIb) the difference is maintained even at room temperature (32.6 and 28.4 p.p.m.):[82]


(XLI, a and b)
R=H (a), CH_3 (b).

The majority of the alkoxycarbenium ions with different substituents at the carbenium carbon atom exist only in the form of one isomer, which can be explained by the difference between the thermodynamic stabilities of the two isomers.[53] However, the simplest ions, such as the chloromethoxycarbenium ions (XLII) and the fluoromethoxycarbenium ion (XLIII), each form two isomers, which have different ^1H NMR spectra (Table 1). The isomers have been identified on the assumption that the *cis*-allyl constant is higher than the *trans*-constant. The ratio of the isomers (XLIIa) and (XLIIb) is 81 : 19, while that of (XLIIIa) and (XLIIIb) is 70 : 30.[52]

Table 1. Characteristics of the ^1H NMR spectra of alkoxycarbenium ions in superacids.

Ion	Solvent	T, °C	δ, p.p.m.*; multiplicity (J, Hz) H¹	H²	H³	Refs.
 (XXIX)	A	−75	9.13; s	9.13; s	5.14; s	[79]
	B	−60	9.66	9.78	5.59	[54]
	C	−60	9.70; d.qr (20.8; 0.9)	9.82; d.qr (20.8; 1.0)	5.63; d.d (0.9; 1.0)	[54]
 (XL)	C	−60	10.06; d.t (18.4; 1.1)	9.99; d.t (18.4; 1.5)	7.02; d.d (1.5; 1.1)	[54]
 (XLIIa)	C	−60	10.90; qr (1.2)	—	5.60 d (1.2)	[52]
 (XLIIb)	C	−60	10.66; qr (0.7)	—	5.72 d (0.7)	[52]
 (XLIIIa)	C	−60	9.76; d.qr (98.0; 1.2)	—	5.46; d (1.2)	[52]
 (XLIIIb)	C	−60	9.86; d.qn (98.0; 0.7)	—	5.64; t (0.7)	[52]
$CH_2\overset{+}{=}OCH_2CH_3$ (XLVII)	A	−75	9.34; s	5.54; qr (7.0)	1.71; t (7.0)	[79]
$CH_2\overset{+}{=}OCH(CH_3)_2$	A	−75	9.25; s	5.78; sp (6.2)	1.65; d (6.2)	[79]
$CH_3CH\overset{+}{=}OCH_3$ (XLIX)	A	−75	9.49; qr (3.5)	2.95; d (3.5)	5.00; s	[79]
	B	−60	9.50 qr.qr (4.0; 0.8)	3.20; d.qr (4.0; 0.8)	5.30; qn (0.8)	[53]
$(CH_3)_2C\overset{+}{=}OCH_3$ (XXXIV)	A	−45	—	2.78; s	4.87; s	[80]
	B	−60	—	3.18; s	5.00; s	[53]
	D	20	—	3.4; s	5.3; s	[76]
$CH_3CH\overset{+}{=}OCH_2CH_3$ (LI)	A**	−75	9.54; qr (3.5)	2.94; d (3.5)	5.36; qr (7.0)	[79]
	B***	−60	9.85; qr (4.0)	3.07; d (4.0)	5.55; qr (7.0)	[53]
$CH_3CH_2CH\overset{+}{=}OCH_3$ (L)	B****	−60	9.90; m	3.60; qr (7.0)	1.25; t (7.0)	[53]
$CH_3CH_2CH\overset{+}{=}OCH_2CH_2$	B*****	−60	9.95; m	3.52; qr (6.5)	1.10; t (6.5)	[53]

Notation. Solvent: A = HSO_3F; B = HSO_3F–SbF_5–SO_2; C = SbF_5–SO_2; D = H_2SO_4–SO_3 (30%). Multiplicity: s = singlet; d = doublet; t = triplet; qr = quartet; qn = quintet; sp = septet; m = multiplet.

*The values of δ in H_2SO_3F have been determined relative to the internal standard CH_2Cl_2 (δ = 5.33 p.p.m.) and have been recalculated relative to TMS; in the remaining cases the recalculation has been relative to an external TMS standard.

**The parameters 1.67; t (7.0) correspond to the signal of the H^4 proton.

***The parameters 1.70; t (7.0) correspond to the signal of the H^4 proton.

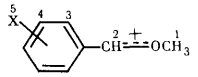
The carbenium and oxonium characters of alkoxycarbenium ions determine their dual reactivity. In most cases, alkoxycarbenium ions react as carbenium ions. For example, the interaction of a solution of the methoxycarbenium ion (XXIX) in the SbF_5–SO_2 mixture with methanol in the presence of K_2CO_3 at −78 °C results in the formation of dimethoxymethane:[52]

$$\underset{\text{(XXIX)}}{CH_2\overset{+}{=}OCH_3} + CH_3OH \xrightarrow[-H^+]{} CH_3OCH_2OCH_3 .$$

An analogous formation of an acetal takes place when a salt of the alkoxycarbenium ion (XLIV) is treated with sodium ethoxide in benzene:[55]

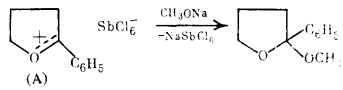
$$\underset{\text{(XLIX)}}{[ClCH\overset{+}{=}C(CH_3)\overset{+}{=}CHOC_2H_5]^+ SbCl_6^-} \xrightarrow[-NaSbCl_6]{C_2H_5ONa} ClCH=C(CH_3)-CH(OC_2H_5)_2 .$$

Table 2. The chemical shifts (δ, p.p.m.) in the ^1H NMR spectra of aryl-substituted alkoxycarbenium ions in HSO_3F at 34 °C (relative to a TMS external standard).[72]



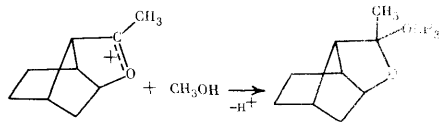
X	H^3	H_2	H^5	H^4	H^5
H	4.78	9.13	—	—	—
p-CH_3	4.71	8.96	8.00	7.44	2.40
p-OCH_3	4.51	8.57	7.94	7.02	3.90
p-Cl	4.71	9.12	8.08	7.56	—
p-Br	4.78	9.13	7.93	7.77	—
p-F	4.78	9.07	—	—	—
p-NO_2	5.01	9.55	8.36	8.36	—
m-F	4.88	9.25	—	—	—
o-CH_3	4.79	9.26	—	—	2.56
o-OCH_3	4.61	9.31	—	—	3.90
o-$CH\overset{3+}{=}OCH_3$	5.16	9.85	—	—	—
m-$CH\overset{+}{=}OCH_3$	5.07	9.62	—	—	—
p-$CH\overset{+}{=}OCH_3$	5.12	9.71	8.44	8.44	—

On treatment with alkoxide anions, cyclic alkoxycarbenium ions also give rise to acetals. When 2-phenyl-2-tetrahydrofurylium hexachloroantimonate was treated with sodium methoxide in methanol, 2-methoxy-2-phenyltetrahydrofuran was obtained:[7]



(A)

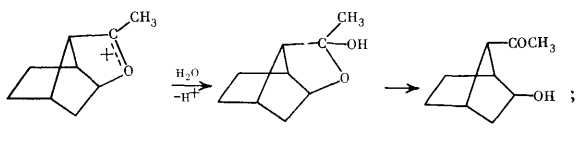
In many cases acetals are formed also when alkoxycarbenium salts are treated with alcohols:[40]

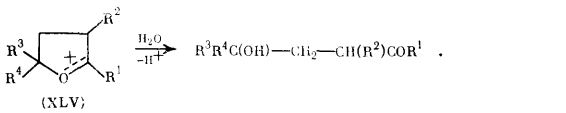


****The parameters 5.30; s correspond to the signal of the H^4 proton.

*****The parameters 5.51; qr (7.0) correspond to the signal of the H^4 proton and the parameters 1.70; t (7.0) correspond to that of the H^5 proton.

Alkoxycarbenium ions react with water also as carbenium ions. The reaction products are unstable hemiacetals, which are then converted into carbonyl compounds:[40,41]

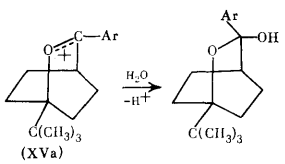




(XLV)

When solutions of alkoxycarbenium ions (XLV) are poured into an aqueous solution of NaOH, γ-hydroxycarbonyl compounds are produced.[34,35]

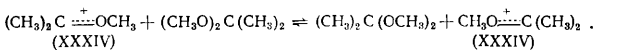
In some cases, hemiacetals have been isolated and characterised:[17]



(XVa)

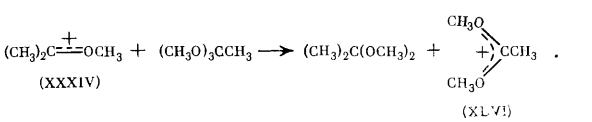
The rate of hydrolysis of alkoxycarbenium ions varies within wide limits depending on their structure.[85]

Alkoxycarbenium ions can react also with weaker nucleophiles such as acetals and orthoesters. Thus, it was noted above that, when acetals are treated with an excess of bromine in SO_2 at −60 °C, alkoxycarbenium ions are formed. In the presence of a deficiency of bromine, the chemical shifts observed in the ^1H NMR spectrum assume intermediate values between those of the acetal and the ion; within the limits of the bromine : acetal ratios from 0 to 1, they vary linearly with the bromine content, but, on further increase of the latter, remain unchanged, which shows that the following rapid equilibrium exists in solution even at −60 °C:[74]



(XXXIV) (XXXIV)

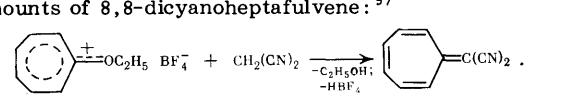
The interaction of the same ion (XXXIV) with methyl orthoacetate leads irreversibly to the formation of the more stable dimethoxymethylcarbenium ion (XLVI) and an acetal:[74]



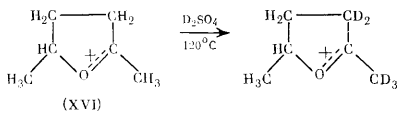
(XXXIV) (XLVI)

The methoxycarbenium ion adds smoothly to double and triple bonds in various compounds.[56–61]

Alkoxycarbenium ions can react with compounds containing an activated methylene group. For example, ethoxytropylium tetrafluoroborate reacts with malonodinitrile in the presence of bases, and together with tropone, gives rise to considerable amounts of 8,8-dicyanoheptafulvene:[97]



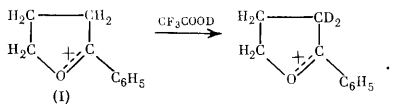
Like other carbenium ions, alkoxycarbenium ions can be stabilised by splitting off a proton from the β-position. Experiments with deuterated sulphuric acid established that the hydrogen atom in the β-positions relative to the carbenium centre in the 2,5-dimethyl-2-tetrahydrofuryl cation (XVI) are substituted by deuterium at 120 °C:[25]



(XVI)

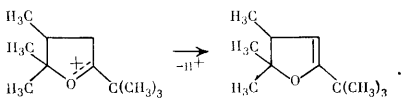
In the analogous cations (XLV) in solution in 96% D_2SO_4 the H–D exchange takes place at 70–100 °C, but is hardly observed at 25 °C. However, on reducing the D_2SO_4 concentration to 80%, the exchange proceeds at an appreciable rate also at 30 °C.[34] Such exchange is effected via deprotonation with the intermediate formation of vinyl ether and its subsequent deuteration.

In a less acidic medium (trifluoroacetic acid) deuterium exchange is observed even at room temperature:[6,7]

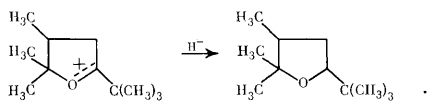


(I)

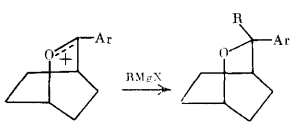
The deprotonation of sterically hindered alkoxycarbenium ions with formation of vinyl ethers becomes the dominant pathway even in reactions such as hydrolysis[32] or interaction with an alkoxide anion:[31,32]



On treatment with hydride ion donors[17,40,41,47] or on catalytic hydrogenation in the presence of Pd/C,[32] alkoxycarbenium ions are reduced to ethers:

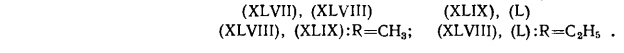


On treatment with Grignard reagents, alkoxycarbenium ions are alkylated:[17]



Under suitable conditions, alkoxycarbenium ions can abstract on alkyl anion from cyclic ketals. It has been suggested that this reaction is responsible for the formation of cyclic dialkoxycarbenium ions (XXXI) on treatment of cyclic ketals with trialkyloxonium salts[69] (see the scheme above).

The most striking manifestation of the carbenium character of alkoxycarbenium ions is their capacity for isomerisation. When ethoxycarbenium hexachloroantimonate (XLVII) and propoxycarbenium hexachloroantimonate (XLVIII) were dissolved in water, considerable amounts of methanol and acetaldehyde or propionaldehyde were formed apparently as a result of the isomerisation of the ions (XLVII) and (XLVIII) via the 1,3-hydride shift to the methoxymethylcarbenium ion (XLIX) or the ethylmethoxycarbenium ion (L), together with the hydrolysis products—formaldehyde and ethyl or propyl alcohol:[98]



(XLVII), (XLVIII) (XLIX), (L)

(XLVIII), (XLIX):R=CH_3; (XLVIII), (L):R=C_2H_5 .

The study of the behaviour of the alkoxycarbenium ions obtained by dissolving formaldehyde acetals in HSO_3F at −70 °C[80,81] showed that ethoxy- and propoxycarbenium ions are stable in HSO_3F up to −30 °C. At higher temperatures signals due to the presence in solution of methanol and also

of the ions (XLIX) and $CH_3CH{=}\overset{+}{O}CH_2CH_3$ (LI) or (L) and $C_2H_5CH{=}\overset{+}{O}C_3H_7$ (LII) appear in the ^1H NMR spectra.

The characteristic signal of the fragment $CH_3O{=}\overset{+}{C}-$ has been detected also in the ^1H NMR spectra of the cyclic formaldehyde acetals in HSO_3F at temperatures above −30 °C.[83]

The ion (XLIX) could be formed from the ion (XLVII) not only via an internal 1,3-hydride shift but also as a result of intermolecular hydride transfer. The abstraction of a hydride ion from the ethyl alcohol present in solution should lead to the formation of ethyl methyl ether and protonated acetaldehyde:

$$\underset{\text{(XLVII)}}{CH_2{=}\overset{+}{O}CH_2CH_3} + CH_3CH_2OH \rightarrow CH_3OCH_2CH_3 + CH_3CH{=}\overset{+}{O}H .$$

Next, the transfer of the hydride ion from the α-position in the ethyl group of ethyl methyl ether to the protonated acetaldehyde or the ethoxycarbenium ion would lead to the methoxymethylcarbenium ion and ethyl alcohol or ethyl methyl ether:

$$CH_3OCH_2CH_3 + CH_3CH{=}\overset{+}{O}H \rightarrow \underset{\text{(XLIX)}}{CH_3O{=}\overset{+}{C}HCH_3} + CH_3CH_2OH ;$$

$$CH_3OCH_2CH_3 + \underset{\text{(XLVII)}}{CH_3CH_2O{=}\overset{+}{C}H_2} \rightarrow \underset{\text{(XLIX)}}{CH_3O{=}\overset{+}{C}HCH_3} + CH_3CH_2OCH_3 .$$

However, specially formulated experiments showed that under these conditions diethyl ether does not react with protonated acetaldehyde or the methoxycarbenium ion:[81]

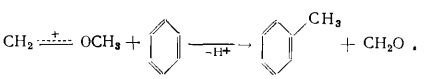
$$CH_3CH_2OCH_2CH_3 + CH_3CH{=}\overset{+}{O}H \not\rightarrow$$

$$CH_3CH_2OCH_2CH_3 + \underset{\text{(XXIX)}}{H_2C{=}\overset{+}{O}CH_3} \rightarrow \underset{\text{(LI)}}{CH_3CH_2O{=}\overset{+}{C}HCH_3} + CH_3OCH_3 .$$

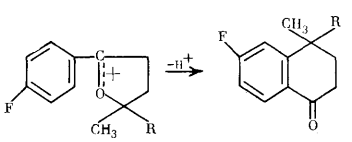
On this basis, it was concluded that the ion (XLVII) is converted directly into (XLIX) via an internal 1,3-hydride shift.[81]

Whereas the 1,3-hydride shift in the ethoxycarbenium ion leads to an energy gain since the ion (XLIX) is more stable to the extent of 46 kJ mol^{-1} than the ion (XLVII),[99] the analogous process in the methoxycarbenium ion is degenerate. The study of the temperature-induced changes in the ^1H NMR spectra and experiments with deuterated dimethoxymethane species showed that the 1,3-hydride shift in the methoxycarbenium ions takes place at 40 °C.[81]

Alkoxycarbenium ions can react as oxonium ions, splitting off an alkyl cation or transferring it to nucleophiles. Thus a methoxycarbenium salt methylates aromatic hydrocarbons:[62]

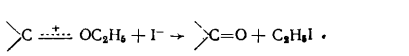


An example of the intramolecular alkylation of an aromatic ring can be provided by the conversion of the ions (Vb) and (VII) into the corresponding tetralones:[9]

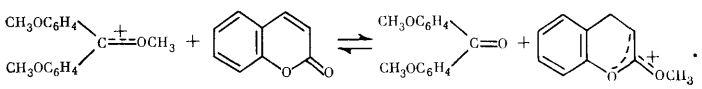


R = H (Vb), CH_3 (VII)

The interaction of alkoxycarbenium ions with iodides results in the alkylation of the iodide ion:[37]



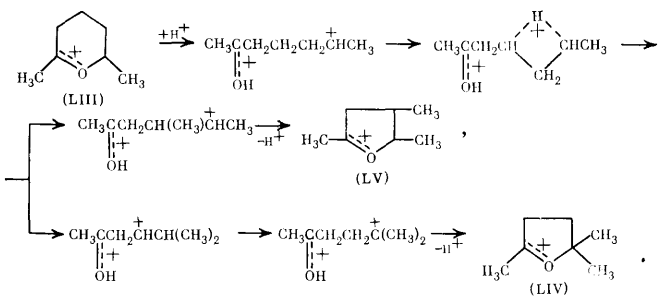
Alkoxycarbenium ions can alkylate also certain oxygen-containing compounds. For example, the interaction of the methoxydi(*p*-methoxyphenyl)carbenium ion with coumarin leads to the formation of an equilibrium mixture:[39]



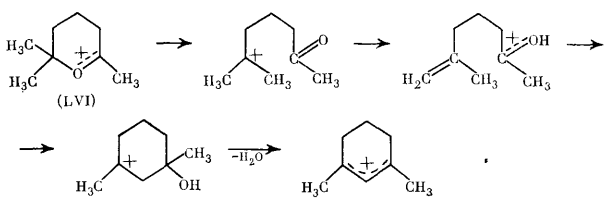
The possibility of the reaction of alkoxycarbenium ions as oxonium ions depends also on the strength of the nucleophile. For example, the cyclic 2-phenyl-2-tetrahydrofuryl cation is stable in trifluoroacetic acid. When sodium trifluoroacetate is added to the solution, the cation reacts with the trifluoroacetate ion to form γ-trifluoroacetoxybutyrophenone:[6]

$$(A) + CF_3COO^- \rightarrow C_6H_5COCH_2CH_2CH_2OCOCF_3 .$$

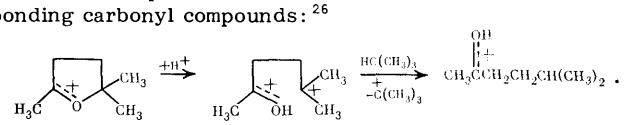
In the absence of nucleophiles the oxonium character of alkoxycarbenium ions is manifested by the possibility of their dealkylation. Thus the ion (LIII), which is stable in superacids at room temperature, is converted into a mixture of the ions (LIV) and (LV) on heating to 100 °C. It has been suggested[28] that this reaction proceeds in accordance with the following scheme:



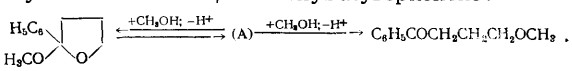
The 6,6-dimethyl-substituted analogue (LVI) is still less stable. In 96% H_2SO_4 the ring is opened in the course of 5 min even at room temperature and a series of reactions lead ultimately to the cyclic allyl cation:[84]



Five-membered cyclic alkoxycarbenium ions without substituents at the carbenium centre undergo an analogous dehydration.[49] In superacid media cyclic alkoxycarbenium ions can abstract a hydride ion from hydrocarbons such as isobutane or isopentane and can be reduced to the corresponding carbonyl compounds:[26]

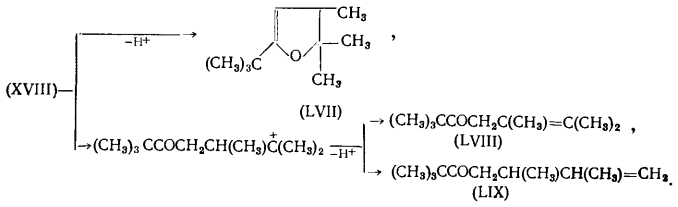


In certain cases the carbenium and oxonium properties of alkoxycarbenium ions are manifested simultaneously. In the reaction of the ion (A) with methanol, the product formed initially is 2-methoxy-2-phenyltetrahydrofuran, which is gradually converted into γ-methoxybutyrophenone:[7]



Such behaviour is due to the fact that in an acid medium the first reaction is reversible and its rate is higher than that of the second reaction. In the initial instant the main product is therefore 2-methoxy-2-phenyltetrahydrofuran—the product of the reaction occurring under the conditions of kinetic control. After a time, the product resulting from thermodynamic control, namely γ-methoxybutyrophenone, accumulates in the mixture.

Three products, compounds (LVII), (LVIII), and (LIX) in the proportions 9 : 2 : 3, have been obtained on heating a mixture of 2-t-butyl-4,5,5-trimethyl-2-tetrahydrofurylium tetrafluoroborate with potassium t-butoxide: [31]



The formation of the first proton (LVII) is due to the carbenium character of the initial ion, while the formation of the other two products (LVIII) and (LIX), is due to its oxonium character.

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Thus alkoxycarbenium ions have now been transformed from hypothetical intermediates into entirely real objects available for study by physical methods. Nevertheless, one cannot claim that these ions have been adequately investigated. The study of alkoxycarbenium ions by modern methods such as ^{1}H, ^{13}C, and ^{17}O NMR, ion-cyclotron resonance, and quantum-chemical calculations will yield more detailed information about their structure and properties, which will in its turn enable chemists to predict their reactivity and to control appropriately the reactions in which they are formed.

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Ufa Petroleum Institute

Translated from *Uspekhi Khimii*, 53, 1548-1571 (1984) U.D.C. 547.492 : 542.934.2

New Trends in the Hydration of Nitriles

E.N.Zil'berman

The advances in the hydration of nitrile ligands in complexes with various central ions, in the employment of complexes as homogeneous catalysts of the hydration of nitriles, and in the addition of water to the nitrile group in the presence of manganese(IV) oxide and other metal oxides as well as catalysts containing metallic copper and other metals are examined. The conditions in the synthesis of amides, the influence of the structure of the starting materials on the mode of reaction and on the side reactions accompanying hydration, the reaction mechanisms, and the practical value of individual pathways leading to the conversion of nitriles into amides are discussed.
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I. INTRODUCTION

The hydration of nitriles is frequently used to prepare the corresponding carboxylic acid amides. The classical hydration procedures are based on the interaction of nitriles with water and hydrogen chloride, sulphuric acid, or other inorganic acids and also on the reaction of nitriles with hydrogen peroxide in aqueous alkali. These and certain other methods have been considered in detail in a monograph[1] covering the literature mainly up to 1970 and have still not lost their importance. However, during the past 10–12 years a number of fundamentally new procedures for the conversion of nitriles into amides have been proposed and have developed rapidly. Thus, advances have been made in the hydration of coordinated nitriles, homogeneous-catalytic hydration using catalysts, mainly complexes, has been achieved and is being improved, and particularly significant results have been obtained in liquid-phase heterogeneous-catalytic hydration of nitriles in the presence of certain metal oxides or metals, which made it possible, in particular, to organise the large-scale manufacture of acrylamide by the hydration of acrylonitrile in the presence of catalysts containing metallic copper.[2]

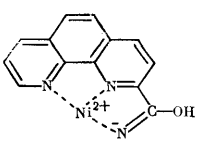
This review deals with the present state of these problems mainly on the basis of the literature up to 1982.

II. HYDRATION WITH FORMATION OF COORDINATED AMIDES

The chemistry of complexes containing nitrile molecules in the inner sphere has attracted much attention.[3] In these complexes the nitriles are as a rule n-coordinated to the central ion but π-complexes are also formed in some cases. The coordination of nitriles results in a sharp increase of their electrophilic reactivity.[3]

The hydration of coordinated nitriles leading to the formation of coordinated amides was first investigated in relation to pyridine derivatives containing the cyano-group in the 2-position, evidently because the amides formed, behaving as bidentate ligands, give rise to relatively stable complexes with many ions, including bivalent cobalt, nickel, copper, and zinc ions; on the other hand, the complexes of these ions with monodentate amide ligands are extremely unstable.

The hydration of 2-cyano-1,10-phenanthroline is greatly accelerated by copper(II) as well as nickel(II) and zinc ions even at room temperature.[4] 1,10-Phenanthroline-2-carboxamide can be isolated quantitatively from the reaction products by treatment with the disodium salt of ethylenediaminetetra-acetic acid. The kinetics and mechanism of the hydration reaction in the presence of salts have been studied and it has been shown that it is of first order with respect to the metal ion complex with the substrate and with respect to hydroxide ions. The second-order rate constant for the reaction catalysed by Ni^{2+} is ~10^7 times greater than for the hydration in the same basic medium but in the absence of metal ions. This acceleration is caused by the appreciable alteration of the entropy of activation (from -50 J mol^{-1} K^{-1} in the absence of nickel to $+59$ J mol^{-1} K^{-1} in its presence). According to the mechanism proposed, the nitrile and Ni^{2+} form a complex in which the CN group is located close to the metal ion but is not coordinated to it; this group is attacked by the OH^- ion with formation of a complex in which Ni^{2+} now interacts with three nitrogen atoms:



The positive entropy of activation is probably associated with the fact that a coordinated water molecule is displaced from the initial nickel complex on formation of the transition state and appreciable desolvation of the nucleophile takes place. The above mechanism is preferred over the alternative mechanism according to which the nitrile group is subjected to the nucleophilic attack by the hydroxo-group coordinated to the central ion and not by a free OH^- ion.[4,5] It is noteworthy that the subsequent hydrolysis of the 1,10-phenanthroline-2-carboxamide formed is also accelerated in the presence of copper(II), nickel(II), and zinc salts but to a much lesser extent than the hydration of the nitrile.[4]

2-Cyanopyridine, coordinated to copper(II) or nickel(II), is rapidly hydrated to pyridine-2-carboxamide on heating in aqueous solutions, the carboxamide remaining bound to the metal ion the form of a chelate compound.[6] The hydration of

2-cyano-8-hydroxyquinoline complexes of nickel(II), cobalt(II), and copper(II) proceeds analogously. In terms of its kinetic features, the reaction differs little from the hydration of coordinated 2-cyano-1,10-phenanthroline examined above. Here too the sharp increase of rate on passing from the free to the coordinated nitrile is associated with the increase of the activation entropy—from −113 to −4 J mol^{-1} K^{-1} in the nickel complex and to −13 J mol^{-1} K^{-1} in the cobalt complex (while the enthalpy of activation remains unaltered).[7,8]

The nitrile group of the *o*-cyanobenzyl ligand coordinated as a bidentate species to platinum(II) [9] and palladium(II) [10] in complexes of the type

$$\left[L_2Pd\begin{matrix}CH_2C_6H_4CN\\NCC_6H_4CH_2\end{matrix}PdL_2\right]^{2+}(BF_4^-)_2\ ,$$

where L_2 = $2PPh_3$, 1,2-bis(phenylphosphino)ethylene, or 1,2-bis(phenylphosphino)ethane, is hydrated at 50 °C in solution in aqueous acetone. It is believed[9] that the reaction begins with the nucleophilic substitution of the coordinated cyano-group by water, after which the water coordinated to the central ion interacts intramolecularly with the ligand containing the cyano-group and occupying the *cis*-position. The *o*-toluidide and complexes of the type PtL_2Cl_2 have been obtained by treating the dimeric carboxamide-complexes with hydrochloric acid.

Cobalt(III) forms with amides much more stable complexes than the bivalent metals examined above. Even complexes with amides without groups capable of forming an additional coordinate bond with the central ion are distinguished by an appreciable stability; different nitrile complexes based on cobalt(III) are therefore conveient objects for a detailed study of hydration. The reaction was first achieved[11] with pentamminecobalt complexes containing benzonitrile and 3- and 4-hydroxybenzonitriles as ligands:

$$[Co(NH_3)_5NCR]^{3+} + OH^- \rightarrow [Co(NH_3)_5NHC(=O)R]^{2+}\ .$$

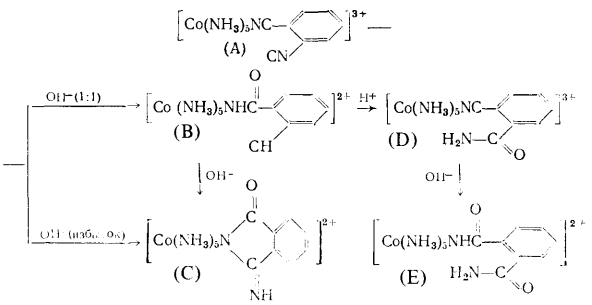
In an acid medium these complexes are reversibly protonated:

$$[Co(NH_3)_5NHC(=O)R]^{2+} + H^+ \rightleftarrows [Co(NH_3)_5NH_2C(=O)R]^{3+}\ .$$

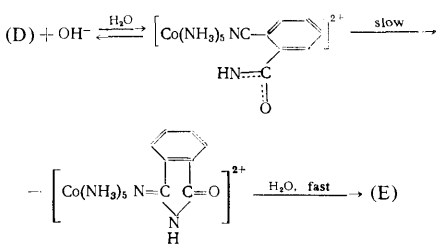
The reaction proceeds analogously also when pentamminecobalt complexes of 3-cyano-, 4-cyano-, 4-acetyl-, 3-formyl-, and 4-formyl-benzonitriles and even 2-, 3-, and 4-cyanopyridines are used.[12,13] The kinetics of the hydration reaction are described by a second order equation—of first order with respect to the complexes and of first order with respect to hydroxide ions. (In the hydration of coordinated formylbenzonitriles the hydration kinetics are complicated by the reversible reaction involving the addition of OH^- ions to the carbonyl group, which takes place simultaneously.[12]) The *n*-coordination of benzonitriles to Co^{3+} makes it possible to increase the rate constants for their hydration by a factor of 10^6–10^7. The rate constants then increase also with increase of the electron-accepting capacity of the substituents in the benzonitrile. The activation parameters for the hydration of coordinated benzonitriles are as follows:[11,12] $\Delta H^{\neq}$ = 51.5–69.1 kJ mol^{-1} and $\Delta S^{\neq}$ = −31–+21 J mol^{-1} K^{-1}. These values of $\Delta S^{\neq}$ are much greater than the $\Delta S^{\neq}$ for the hydration of non-coordinated benzonitriles.

The nitrile group is hydrated under mild conditions and with low yields also in the pentamminecobalt(III) complexes of acetonitrile[14] and acrylonitrile.[15]

The neighbouring functional groups can exert a significant influence on the hydration of the nitrile coordinated to a transition metal. In particular, interesting results have been obtained in the hydration of 1,2-dicyanobenzene coordinated to cobalt(III).[16] The pentamminecobalt complex of the dinitrile (A) reacts with a stoichiometric amount of a base to form the cyanobenzamide complex (B), which cyclises in the presence of an excess of the base to the 3-imino-1-oxoisoindoline complex (C). Coordination, which sharply accelerates the reaction (A) + OH^- – (B), has very little influence on the rate of cyclisation. In an acid medium the complex (B) undergoes an intramolecular rearrangement with formation of the complex (D), in which the nitrile group is coordinated to the cobalt atom, while the amide group is free. In the presence of a base, this nitrile complex is hydrated to the phthalamide complex (E). The rate constant for the last reaction is 10^3 times greater than the rate constant for the reaction (A) + OH^- → (B).



Detailed study of the kinetics of the hydration of coordinated dicyanobenzenes and 2-cyanobenzamide made it possible to refine the mechanism of the catalysis of the hydration of the nitrile group under the influence of the neighbouring carboxamide group in the complex (D).[17] Since the rate of hydration of 1,2-dicyanobenzene is only ~3 times greater than the rate of hydration of 1,3- and 1,4-dicyanobenzenes, it was concluded that the *o*-nitrile group influences the reactivity of the coordinated CN group in the complex (A) solely by virtue of its electron-accepting capacity. On the other hand, the appreciable increase of the rate of reaction in the complex (D) under the influence of the less electron-accepting *o*-carboxamide group shows that the latter influences the hydration via another mechanism. The entropy of activation for hydration in the complex (A) (+4 J mol^{-1} K^{-1}) is of the same order of magnitude as for other complexes of the nitriles in the inner sphere (−31–+21 J mol^{-1} K^{-1}), while the activation entropy for hydration in the complex (D) is unusually high (+184 J mol^{-1} K^{-1}). On the basis of these data and bearing in mind that the hydration of the CN group and the complex (D) is catalysed specifically by OH^- ions, a reaction mechanism has been proposed according to which the amide group is initially deprotonated and this is followed by the inner-sphere nucleophilic attack on the CN group with formation of an isoindole heterocycle, which hydrolyses to compound (E):



According to Balahura and Purcell,[17] the high value of $\Delta S^{\neq}$ is due to the desolvation of both the OH^- ion and the carboxamide anion together with the partial neutralisation of the

charge on cyclisation. Thus the high rate of hydration of the CN group in the complex (D) can be explained by the combination of the effects of coordination and catalysis by the o-carboxamide group.

The coordination of nitriles leads not only to an increase of the electrophilic reactivity of the CN group but also to an appreciable increase of the mobility of the α-hydrogen atoms of the nitrile ligand. Under the conditions of the hydration of coordinated acetonitrile is an alkaline medium, this is expressed by the simultaneous exchange of the protons of the methyl group.[14] The coordination of malononitrile, cyanoacetic acid, and its ethyl ester to pentamminecobalt(III) leads to such a sharp increase of the acidity of these compounds that in aqueous alkaline solutions equilibrium is rapidly established between the initial complexes and complexes containing the deprotonated methylene group. In these systems the initial complexes are hydrated through both OH^- ions and water while in the coordinated carbanions an electron is displaced with formation of the cobalt(II) ion and the corresponding free radical:[15,18]

$$[Co(NH_3)_5(NCCH_2CN)]^{3+} \begin{cases} \xrightarrow{OH^-} [Co(NH_3)_5(NHCCH_2CN)]^{2+}, \\ \xrightarrow{H_2O} [Co(NH_3)_5(NHCCH_2CN)]^{2+} + H^+, \\ \xrightarrow[-H_2O]{OH^-} [Co(NH_3)_5(NCC^-HCN)]^{2+} \rightarrow Co^{2+} + 5NH_3 + NC\dot{C}HCN. \end{cases}$$

The free radicals formed as a result of the reaction of the ligands in a non-aqueous medium initiate the polymerisation of acrylic monomers and styrene.[15]

The hydration of nitriles bound as ligands to the central ion in the pentammine complexes of platinum group metals has been described in a number of studies.[19–21] In weakly alkaline solutions the reaction proceeds at a high rate, which is proportional to the concentrations of both the complex and OH^- ions. The pentammineruthenium(III) complexes of acetonitrile and benzonitrile are hydrolysed ~10^8 times faster than the free nitriles and ~10^2 times faster than the pentamminerhodium(II) complexes of the same nitriles. In the corresponding ruthenium(II) complex of acetonitrile the reaction is ~10^6 times slower than in the ruthenium(III) complex. The high reactivity of the ruthenium(III) complex can be explained by the fact that the ruthenium(III) ion, which is a powerful π-electron acceptor, stabilises the negative charge formed on the ligand as a result of attack by the hydroxide anion on the carbon atom of the nitrile group. The comparatively low reactivity of the ruthenium(II) complex is associated with the fact that in this instance the central ion is a weak π-electron acceptor. It has been found that in hydration in a weakly alkaline medium (pH 8–9) the complex $[Ru(NH_3)_5NCPh]^{3+}$ undergoes a side reaction to a slight extent, namely the disproportionation to the ruthenium(II) and ruthenium(IV) complexes.[20] According to Diamond and co-workers,[22,23] ethyl cyanoacetate and αβ-unsaturated nitriles coordinated to ruthenium(III) are also hydrated to the corresponding amides.

The rate constants for the reactions of the pentamminerhodium(III) and pentammineiridium(III) complexes of benzonitrile with OH^- ions have been determined.[21] Comparison with the reaction of the corresponding cobalt(III) complex under analogous conditions[11] showed that the rate constants decrease in the sequence Co > Rh > Ir, i.e. in the homologous series of complexes with the same central ion electron configuration completion the reactivity decreases with increasing the ionic radius. This confirms the significant influence of the electrostatic attraction between the central ion and the nitrile ligand on the ability of the latter to be subjected to nucleophilic attack.[21]

As a consequence of the high stability of cobalt(III), ruthenium(III), and other tervalent metal complexes[22–25] of carboxylic acid amides, the isolation of the free amides requires the reduction of the central ion in these complexes to the II-state, which gives much less stable complexes. A method has also been proposed[22–24] for the preparation of amides from pentammineaquoruthenium(II) trifluoroacetate and nitriles in accordance with the scheme

$$[Ru(H_2O)(NH_3)_5]^{2+} + RCN \xrightarrow[-H_2O]{} [Ru(NH_3)_5NCR]^{2+} \xrightarrow[-e]{} [Ru(NH_3)_5NCR]^{3+} \xrightarrow{H_2O} \rightarrow$$

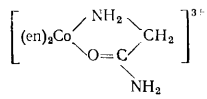
$$\rightarrow [Ru(NH_3)_5NH_2\overset{O}{\overset{\|}{C}}R]^{3+} \xrightarrow{+e,H_2O} [Ru(NH_3)_5(H_2O)]^{2+} + RCONH_2.$$

The addition of water to acetonitrile and benzonitrile coordinated to platinum(II) in the *trans*-acetonitrilebis(triphenylphosphino)methylplatinum cationic complex in an alkaline medium has been described.[26] Analogous results were obtained later[27] starting with similar complexes having other tertiary phosphine ligands:

$$[PtMe(NCMe)L_2]^+ \xrightarrow{H_2O,OH^-} PtMe(\overset{O}{\overset{\|}{H}}NCMe)L_2.$$

The interaction of $[PtCl_4]^{2-}$ with acetonitrile combined with the oxidation of the central ion by oxygen leads to the formation of the acetamide complex of platinum(IV). It has been suggested[28] that the reaction proceeds via the intermediate formation of the complexes $[Pt(NCMe)Cl_3]^-$ and $Pt(H_2O)\cdot(NCMe)Cl_2$.

Studies of the hydration of the nitrile group incorporated in the inner sphere of a complex but not linked directly to the central ion are of interest. It has been shown[29] that the CN group of the aminoacetonitrile ligand in the complex *cis*-$[Co(H_2O)(en)_2(H_2NCH_2CN)]^{3+}$ is hydrated in neutral and alkaline media with formation of a five-membered chelate compound:



The reaction is regarded as a process within the complex involving hydration by the water molecule coordinated to the cobalt ion. In the analogous complex based on 3-aminopropionitrile hydration does not occur under these conditions and the corresponding six-membered chelate compound is not therefore formed. In an acid medium the complexes of both nitriles are hydrated, but the rate of hydration of the first is ~10^5 times greater. The presence of mercury(II) ions makes it possible to increase the rate of hydration of the aminoacetonitrile and 3-aminopropionitrile ligands to the same extent (by a factor of ~10^7). The different types of behaviour during hydration of aminoacetonitrile and 3-aminopropionitrile incorporated in complexes shows that the presence of the nitrile and water in the same coordination sphere is not a sufficient condition for hydration within the complex; the appropriate disposition of the reacting groups in space is also necessary (in the case considered there must be a possibility of the formation of a five-membered chelate compound). The combination of the accelerating effect induced by the possibility of chelation and of the presence of mercury ions permits, overall, an increase in the rate of hydration in a neutral medium by a factor of 10^{15}–10^{18}. The catalysis by mercury(II) ions can be explained by the fact they they form a complex with the nitrile group, withdrawing electron density to themselves: this facilitates nucleophilic attack by the hydroxide ion and the formation of an unstable Hg^{2+} complex with the amide group.[30] The Ag^+ ion is a less effective catalyst of hydration within the complex, but it is in its turn greatly superior to Zn^{2+} and Cd^{2+}.[29]

The hydration of the nitrile group in the presence of mercury(II) ions in the complexes *cis*-$[Co(en)_2(H_2NCH_2CH_2CN).X]^{2+}$, where X = Cl or Br, is based on the removal of a halide ion under the influence of Hg^{2+}, the occupation of the liberated coordination site by the OH^- ligand, and subsequent catalysis by the Hg^{2+} ion of the nucleophilic attack by the OH ligand on the nitrile group within the complex and the formation of a chelate compound. In the analogous complexes based on aminoacetonitrile the hydration also proceeds partly via this mechanism.[25,29,31]

In the absence of Hg^{2+}, the complexes $[Co(en)_2(H_2NCH_2CN).X]^{2+}$ (at pH 7.3 and above) are not hydrated; instead, rapid intramolecular addition of the deprotonated amino-group, located *trans* to the halide ion and to the non-coordinated nitrile group takes place and complexes in which the amidine substituent has a coordination capacity of three are obtained: $\{Co(en)[H_2NCH_2C(NH_2)=NCH_2CH_2NH_2]X\}^{2+}$. The reaction is of first order with respect to both the initial aminoacetonitrile complex and OH^- ions.[31,32]

III. HOMOGENEOUS-CATALYTIC HYDRATION

It was stated above that bivalent cobalt, nickel, and copper chelate complexes of pyridine-2-carboxamide and other amides with similar structure are extremely stable under the conditions of their synthesis. However, conditions have been found under which the amide ligands in these complexes are substituted by nitriles, which makes it possible to employ such complexes as hydration catalysts.

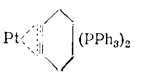
Bivalent nickel, copper, and cobalt complexes of picolinic acid or its amide[33–35] proved to be effective and highly selective catalysts of the hydration of 2-cyanopyridine (pH 5.5 to 8.5, reaction temperature 60 °C and above). In most cases the catalysts remained unchanged after the reaction. The same complexes showed no catalytic activity when an attempt was made to hydrate 3- and 4-cyanopyridines. On the other hand, 2-cyanopyridines are not hydrated in the presence of cobalt(III) and platinum(IV) complexes, although the former reacts with 2-cyanopyridine on heating in aqueous solution.[35] The catalysis of the hydration of 2-cyanopyridine is evidently based on the displacement of the 2-carboxypyridine or pyridine-2-carboxylate ligand from the complex by a 2-cyanopyridine molecule, the subsequent hydration of the coordinated nitrile, and the repeated substitution of the amide ligand formed by the nitrile.[35]

The complex used as the hydration catalyst can be formed in the reaction mixture *in situ*. It is obtained using as the starting material the salts of metals† capable of giving rise to complexes with 2-carboxypyridines and their derivatives. Thus, when aqueous solutions of 2-cyanopyridine[33] and also 4-substituted 2-cyanopyridines[38] were heated with a large excess of nickel(II) or copper(II) chloride, chelates were obtained in which two molecules of the corresponding pyridine-2-carboxamide were present as ligands for each central ion. In the presence of a smaller amount of metal chloride, free amides are also produced together with the chelate complexes. The formation of a chelate complex which catalyses hydration directly also accounts for the conversion of 2,6-dicyanopyridine into pyridine-2,6-dicarboxamide when a mixture of this dinitrile and water is boiled in the presence of catalytic amounts of cobalt(II) acetate.[39]

A study of the hydration of substituted 2-cyanopyridines in the presence of the complex $[Cu(H_2O)(en)_2]Cl_2$ in a nearly neutral medium established that the reactivity decreases in the sequence[38] 2-cyano-4-methylpyridines > 2-cyanopyridine > 2,4-dicyanopyridine. Since an electron-donating substituent in the 4-position promotes and an electron-accepting substituent hinders hydration, it can be assumed that the rate-limiting stage of the process is the nucleophilic reaction involving the incorporation of the nitrile in the inner sphere of the complex. 2-Cyanoquinoline proved to be much less reactive than 2-cyanopyridine, apparently because of the lower capacity of the nitrogen atom of the pyridine ring to form a coordinate bond with the central ion. Whereas the 2-cyano-group in 2,4-dicyanopyridine is selectively hydrated while the 4-cyano-group is inert, in 2,6-dicyanopyridine both cyano-groups react and the product is pyridine-2,6-dicarboxamide. It is noteworthy that an increase of temperature (up to boiling of the reaction mixture) and of the duration of heating of aqueous solutions of nitriles and complex catalysts leads to the hydrolysis of pyridinecarboxamides and the formation of the corresponding carboxylic acids.[38]

Thus the hydration of nitriles with the cyano-group in the 2-position in the pyridine ring in the presence of certain bivalent metal complexes can be used to synthesise the corresponding amides. There is so far little information about the successful homogeneous catalytic hydration of other nitriles in the molecules of which there are no groups capable of chelating the ligands.

In the presence of catalytic amounts of zerovalent platinum complexes of phosphines and cyclohexyne, for example,



acetonitrile is converted into acetamide in a low yield after prolonged heating.[26,40] Benzonitrile is hydrated analogously.[40] It has been suggested that a coordinated hydroxo-group, appearing in the platinum complex under the reaction conditions, is responsible for the catalysis. Phenylacetonitrile,[26] which is a stronger CH acid than acetonitile, is not hydrated under these conditions and is merely incorporated in the inner sphere of the complex $Pt(C_6H_9)[CH(CN)Ph](PPh_3)_2$. When non-ionic phosphonocyclohexyne complexes of platinum react with αβ-unsaturated nitriles, the complexes exhibit a capacity to catalyse the addition of water to the C=C bond. Mainly di(2-cyanoethyl) ether and 3-hydroxyproprionitrile and only 8% of acrylamide have been obtained from acrylonitrile.[26]

The strong hydroxo-bases, formed when zerovalent platinum complexes of phosphines, for example $[Pt(P(t\text{-}Bu)_2Ph]_2$ and $Pt[P(iso\text{-}Pr)_3]_3$, are treated with water, were found to catalyst nitrile hydration.[41] After the reaction, the catalysts are isolated and changed. It has been suggested that complexes containing nitriles coordinated to platinum in the corresponding amido-complexes formed from them as a result of attack by OH^- ions are intermediates in the reaction. The degree of conversion of the initial nitriles is low and in the hydration of αβ-unsaturated nitriles the addition of water is not regioselective; in a number of cases the hydration of the C=C bond predominates. Under the conditions of acrylonitrile hydration, the dimer $CH_2=C(CN)CH_2CH_2CN$ was also formed.

† The metal salts are not usually catalysts of nitrile hydration, although it has been reported that various amides have been obtained from nitrile complexes with $PdCl_2$ on boiling with water[36] and also on treatment of solutions of nitriles in acetic acid with $TiCl_4$ and water.[37] However, it is noteworthy that the mechanisms of these reactions have not been studied, so that it is not clear to what extent the complexes and the hydrogen chloride, produced by the hydrolysis of $PdCl_2$ and $TiCl_4$ are each responsible for the hydration.

The hydration of acetonitrile at 80 °C in the presence of different hydroxophenyl and hydroxomethyl complexes $PtRL_2(OH)$ and the analogous acetamido-complexes $PtRL_2$. .(NHCOMe) has been described.[42] The phenyl complexes are more active than the methyl complexes. When R = Ph, the activity of the complexes decreases in the following sequence as a function of the nature of the ligand L:

$$PEt_3 > P(t\text{-}Bu)Me_2 > PPh_3 \simeq PMe_2Ph > P(t\text{-}Bu)_2Me \gg P(C_6H_{11})_3 .$$

When the catalytically most active complex $PtPh(PEt_3)_2(OH)$ was used, 173 moles of acetamide per mole of the catalyst were obtained for a low degree of conversion of acetonitrile (~11%). Under the same conditions, acrylonitrile gives rise to products of the hydration of both the C≡N and C=C bonds. Higher saturated aliphatic nitriles and benzonitriles are hydrated to a lesser extent than acetonitrile, partly because of the inhomogeneity of the reaction medium. Methyl cyanoacetate reacts with the above hydroxo-complexes, forming methoxycarbonyl(keten imino)- or cyanomethoxycarbonylmethyl complexes, for example:

$$PtPh(PEt_3)_2(N{=}C{=}CHCOOMe) \text{ or } Pt(Me)(dppp)[CH(CN)COOMe] ,$$

where dppp = 1,3-bis(diphenylphosphino)propane.

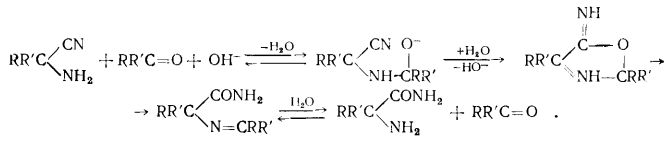
The catalytic hydration of benzonitrile has been carried out also in the presence of the cationic complex $[cis\text{-}Pt(PPh_3)_2.(o\text{-}CH_2C_6H_4CONH_2)]_2(BF_4)_2$. However, not more than 5 moles of benzamide were then obtained per mole of the catalyst. It has been shown[9] that the loss of catalytic activity in the given system is associated with the conversion of the initial complex into the complex $[cis\text{-}Pt(PPh_3)_2(o\text{-}CH_2C_6H_4CONH)]_2$.

The phosphine complexes of zerovalent rhodium and iridium, *trans*-$Rh(CO)(PPh_3)_2(OH)$ and *trans*-$Ir(CO)(PPh_3)_2(OH)$, are more active in the hydration of acetonitrile than the analogous phosphine complexes of platinum. In the presence of the iridium complex, nitriles such as phenylacetonitrile, acrylonitrile, and crotononitrile are also hydrated to the amides.[40]

An appreciable increase of the yields in the homogeneous-catalytic hydration has been achieved in a number of studies.[43–45] The authors began with the results of a study[46] according to which acetonitrile is hydrated to acetamide in a satisfactory yield and with a high selectivity in the presence of sodium chloropalladate and 2,2′-bipyridyl (bipy) at pH 10.4. It was shown[43] that a number of products of the reaction of sodium chloroplatinate [chloropalladate?] and 2,2′-bipyridyl, among which the neutral complex $Pd(bipy)Cl_2$ proved to be a most active catalyst of the hydration reaction are formed under the reaction conditions. Treatment of this complex with an equivalent amount of hydroxide ion yielded the complex $Pd(H_2O)(bipy)(OH)Cl$, which exhibits an even higher catalytic activity. The latter is retained when the chloride ion in the palladium complex is replaced by other anions ($MeCOO^-$, Br^-, OH^-) and bipyridyl is replaced by other bidentate nitrogen-containing ligands.[44] The hydration (at 76 °C and pH 5.5) of acetonitrile and butyronitrile in the presence of an excess of water and catalytic amounts of the above complexes afforded the amides in yields of 70–84% for a selectivity of 100%. The yields of adipamide, benzamide, and phenylacetamide in the hydration of the corresponding nitriles are low. Acrylamide is formed in 80% yield from a heterogeneous mixture of acrylonitrile and water at 60 °C in the presence of a catalytic amount of the complex $Pd(H_2O).(bipy)(OH)_2$ soluble in the nitrile.[45] In order to isolate the amide from the reaction mixture, the catalyst was decomposed with acid, the precipitated complex of the palladium salt of this acid and bipyridyl was filtered off, and the filtrate was evaporated. Study of the hydration kinetics of acetonitrile has established[44] that the amide formed inhibits the addition of water to the nitrile group. The results also support the view that the hydration involves the intramolecular attack by the OH group on the coordinated CN group.

Dichlorobis(η-cyclopentadienyl)zirconium apparently catalyses the hydration of α-hydroxyisobutyronitrile.[118]

Hydration specific to α-aminonitriles, which proceeds in an alkaline medium and is catalysed by carbonyl compounds, has been described. The reaction has been studied in relation to a series of α-aminonitriles with the amino-group at a secondary or tertiary carbon atom, acetaldehyde, isobutyraldehyde, acetone, etc. being used as the carbonyl compounds.[47–49] A carbonyl compound can be formed directly in the reaction mixture together with ammonia and hydrocyanic acid as a result of the hydrolytic decomposition of the α-aminonitrile. The hydration reaction proceeds in accordance with the following mechanism:



Its rate is determined by the rates of the reversible formation of the geminal aminoalkoxide anion and subsequent cyclisation to a substituted 5-imino-oxazolidine. The rate of cyclisation (in the presence of isobutyraldehyde as the catalyst) is then ~10^8 times higher than the rate of nucleophilic attack by OH^- ions on the nitrile group, which is the reason for the catalytic effect of carbonyl compounds.[49] Hydrolysis of the reaction mixtures (without the isolation of the α-aminoamides) makes it possible to obtain α-aminoacids in almost quantitative yields.[50]

IV. HETEROGENEOUS-CATALYTIC HYDRATION

The heterogeneous-catalytic hydration of nitriles can take place in the presence of acids or bases insoluble in the reaction mixture. Anion-exchange resins were frequently used previously as catalysts and 3- and 4-cyanopyridines were hydrated. Under these conditions, 85–96% of 3-cyanopyridine is converted into the amide. The subsequent hydrolysis results in the simultaneous formation of 3-carboxypyridine bound chemically to the catalyst (up to 5–10%), which lowers its activity and necessitates its periodic regeneration.[1,51–55] Attention is concentrated below on new trends in the hydration of nitriles in the presence of heterogeneous catalysts whose action is not based on their acidity and basicity (or not solely on these factors) but on other properties.

1. Hydration in the Presence of Metal Oxides

Among metal oxides, manganese(IV) oxide is the most effective catalyst of the hydration of nitriles. As early as 1934, the formation of benzamide was observed when benzonitrile came into contact with active MnO_2 at room temperature.[56,57] It was suggested[57] that the reaction proceeds by virtue of the water bound to MnO_2 and that the yield of the amide (~3%) is limited by its content. Subsequently the hydration was carried out in methylene chloride[58] and dioxan[59] in the presence of a large amount of MnO_2 containing sufficient bound water to satisfy the stoichiometry of the reaction. It was not until the 1970's that it was established that manganese(IV) oxide is the catalyst and that there is no necessity for its preliminary "saturation" with water for effective hydration.[60,61]

The study of the hydration of benzonitrile in the presence of the β- and γ-modifications of MnO_2 showed that the activity of the catalyst is not determined by its crystal lattice type but by its specific surface,[62] which is usually 30–80 $m^2 g^{-1}$. The catalytic activity of MnO_2 depends on its method of preparation[55] in so far as the conditions of the synthesis influence the surface area of the oxide. The catalyst is used in a powdered or pelleted form. Because of the low degree of coverage of the manganese(IV) oxide surface by the nitrile in the hydration reaction,[63] the yield of the amide per unit mass of the catalyst and per unit time is low and for this reason a comparatively large amount of MnO_2 is used to synthesise the amides, its mass in the hydration reaction carried out by the periodic method usually exceeding severalfold the mass of the nitrile.

Aromatic nitriles, including *o*-substituted nitriles, and water, taken in molar proportions of 1 : 1.2 at 100–140 °C in the presence of MnO_2, form amides in high yields. Hydrolysis takes place to a very slight extent (1–2%),[60,64] but on raising the temperature the yield of the acid increases (it reaches 28% in the reaction with benzonitrile at 200 °C). Aromatic nitriles are hydrated extremely smoothly also in organic solvents—methylene chloride[58] and dioxan.[59]

Halogenoacetonitriles are hydrated to the amides in the presence of MnO_2 in high yields and with a high selectivity at temperatures below 100 °C. At higher temperatures side reactions play a significant role. Thus the hydration of trichloroacetonitrile yielded, together with the amide, appreciable amounts of ammonia, hydrogen chloride, carbon dioxide, and chloroform. The formation of the last compound can be accounted for by the hydrolysis of trichloroacetamide, the decarboxylation of the trichloroacetate anion, and the reaction of the trichloromethyl anion with water.[64]

The hydration of aliphatic nitriles in the presence of MnO_2 in the presence of small amounts of water proceeds to an appreciable extent only on heating to 140–170 °C.[60,64] This results in low yields of amides contaminated by products of side reactions—hydrolysis and oxidation.[65] (The simultaneous reduction of Mn^{4+} to Mn^{2+} leads to the deactivation of the catalyst.) The formation of NH_3 and CO_2 on hydration of acetonitrile is caused mainly by the hydrolysis of acetamide and subsequent "oxidative decarboxylation"[66] of acetic acid:

$$MeCN \xrightarrow{H_2O} MeCONH_2 \xrightarrow[-NH_3]{H_2O} MeCOOH \xrightarrow[-H_2O]{O} [HOOCCOOH] \xrightarrow{O} 2CO_2 + H_2O .$$

Slow acetamide and acetonitrile oxidation reactions also take place and the oxidation of acetonitrile results in the formation of hydrogen cyanide and carbon dioxide. In the hydration of isobutyronitrile the main side products are hydrogen cyanide and acetone, which are formed via α-hydroxyisobutyronitrile; acetone is also formed in the oxidation and decarboxylation of α-hydroxyisobutyric acid.[65]

Satisfactory yields of amides derived from unsubstituted and β-hydroxy- and β-methoxy-substituted aliphatic nitriles are achieved as a result of hydration in the presence of MnO_2 under mild conditions (60–80 °C) in dilute aqueous solutions.[61,67]

When the nitriles are sparingly soluble in water, the initial reaction mixtures are homogenised by organic solvents or the reaction is carried out in the presence of emulsifying agents.

The hydration of succinonitrile in dilute aqueous solutions results in the initial formation of 3-cyanopropionamide, which then combines with a water molecule and is converted into succinamide. Conditions have been found under which each of these compounds is obtained in a high yield.[67] At 60 °C, the rate constants for the addition of the first (activation energy 56 kJ mol^{-1}) and second water molecules are in the ratio 4 : 1. This ratio shows that the influence of the substituents in both reactions is based mainly on the inductive effect. On the other hand, the direct influence of the neighbouring $CONH_2$ group, which leads to a significant alteration of the rate (as for 2-cyanobenzamide coordinated to cobalt[16]), and what is more to a change in the reaction pathway (as in the hydration of succinonitrile in the presence of a copper-containing catalyst[68]), is not observed. At the same time the influence of substituents in the molecules of nitriles on their reactivity is not caused solely by polar effects.[63,67] Thus the effective rate constants (at 60 °C) for the hydration of 3-cyanopropionamide, 3-hydroxypropionitrile, and 3-methoxypropionitrile are in the proportions 2.1 : 1.3 : 1, although the polar constant $\bar{\sigma}^*$ for all three substituents are similar (1.75, 1.60, and 1.73).[69] The causes of the above ratios will be examined below in the discussion of the hydration mechanism.

Under the influence of MnO_2 both in the presence of small amounts of water and in its absence, acrylonitrile and methacrylonitrile partially polymerise via the C=C bonds. In the macromolecules of the polymer based on methacrylonitrile, amide groups as well as short conjugated segments $(\rangle C{=}N{-})_n$ were identified together with the nitrile groups. It has been suggested[64] that the polymerisation proceeds via a radical mechanism and is initiated directly by the free radicals formed as a result of the oxidation of organic compounds by manganese oxide.[70] Acrylamide has been obtained as the main reaction product (70%) from acrylonitril in aqueous solution in the presence of a radical reaction inhibitor, but under these conditions, too, side reactions involving oxidation by manganese oxide take place, which leads to the rapid deactivation of the oxide.[71]

The nitrile groups of polyacrylonitrile in an aqueous solution of potassium thiocyanate at 80 °C are hydrated in the presence of MnO_2 (a degree of conversion of 50% has been achieved).[72]

3-Cyanopyridine in aqueous solution at 85 °C in the presence of MnO_2 is converted into nicotinamide, a product of practical importance, in a high yield (96%). Under the proposed conditions, the reaction takes place in the kinetic region and is described satisfactorily by a first order equation.[62] Similar results were later obtained in other studies[55,73] for the hydration of 3-cyanopyridine in the presence of MnO_2. The cyano-group of cyanamides is hydrated in aqueous solutions in the presence of the same oxide.[74,75]

When phenyl- and diphenyl-acetonitriles were heated with water and MnO_2, the corresponding amides were not obtained because the oxidation reactions predominated.[76] A polymer, soluble in organic solvents, whose molecules incorporated the conjugated (C=N−) chains as well as amide, nitrile, and carboxy-groups, was formed from phenylacetonitrile in the presence of MnO_2 at 80–125 °C (the reaction mechanism has been published[76]). Oxidation of diphenylacetonitrile, having only one hydrogen atom in the α-position, with manganese oxide afforded a high yield of tetraphenylsuccinonitrile.[76]

α-Hydroxynitriles whose OH groups are located at a primary or secondary carbon atom are hydrated selectively and in high yields to α-hydroxyamides in dilute aqueous or aqueous dioxan solutions at room temperature in the presence of MnO_2.[77] An increase of reaction temperature promotes the hydrolysis of the amides formed. Attention has been drawn to the appreciable adsorption of α-hydroxyamides on manganese(IV) oxide. The reactivity of the α-hydroxynitriles RCH(OH)CN decreases in the following sequence in terms of the substituent R: H > Me > Et > n-Pr > iso-Pr. The hydration of α-hydroxynitriles which are tertiary alcohols proceeds in a more complex manner. The hydroxynitriles undergo simultaneous dehydrocyanation under the reaction conditions,[78] which lowers the yield of α-hydroxyamides.

Since α-hydroxyisobutyramide, formed on hydration of α-hydroxyisobutyronitrile, can be used as the starting material for the synthesis of methacrylic monomers,[79–81] most attention has been devoted to the study of the reactions of this nitrile.[63,82,119] It has been found that dehydrocyanation, which is reversible in the absence of MnO_2, becomes almost irreversible in the presence of this oxide. The hydrocyanic acid formed is rapidly adsorbed on the surface of manganese(IV) oxide and is then comparatively slowly oxidised to cyanogen, which gives rise to oxamide on hydration. Under dehydration conditions, dehydrocyanation proceeds until the attainment of equilibrium over a period shorter than 5 min. In the course of approximately the same time, adsorption equilibrium is established between the dissolved hydrocyanic acid and the hydrocyanic acid on the surface of MnO_2. The hydration of α-hydroxyisobutyronitrile as well as the oxidation of HCN take place much more slowly, i.e. the dehydrocyanation and adsorption period in the main separated in time from the hydration and oxidation period. In the hydration of α-hydroxyisobutyronitrile in an aqueous medium the yield of amide does not therefore exceed 70%. When the reaction is carried out in a less polar medium (in aqueous dioxan solutions), where the dehydrocyanation is appreciably retarded, it is possible to increase the yield of α-hydroxyisobutyramide. The addition of acetone to the reaction medium, which shifts the equilibrium towards hydrocyanation with reformation of the starting material, is even more effective. An important feature of the hydration in the presence of acetone is the presence of an extremum in the relation between the effective rate constants and the water content in the aqueous acetone mixture (there is a minimum at a water mole fraction of 0.8), which can be attributed to a change in the internal structure of the water–acetone mixture.[82] The optimisation of the process taking into account its inhibition by the α-hydroxyisobutyramide formed (adsorption on MnO_2) revealed the conditions (45 °C, 1.3 M nitrile, 3.4 M acetone, 7–8 h) under which α-hydroxyisobutyramide is obtained in 95% yield with a selectivity of 96% in the presence of the catalyst specimen employed. The shift of the dehydrocyanation equilibrium by the introduction into the reaction mixture of the ketone formed as a result of the reaction is effective also in the hydration of other α-hydroxynitriles unstable in water.[63,82]

In aqueous solutions in the presence of manganese(IV) oxide, α-aminoisobutyronitrile is converted into α-aminoisobutyric acid, α-aminoisobutryamide, α-hydroxyisobutyramide, acetone, ammonia, hydrocyanic acid, and its oxidation products. Evidently the hydration of α-aminoisobutyronitrile is accompanied by the hydrolysis of both this compound and of the hydration product as well as secondary reactions of the hydrolysis products:[63]

$$Me_2C(NH_2)CN \left\{ \begin{array}{l} \xrightleftharpoons[-NH_3]{H_2O} Me_2C{=}O + HCN \rightleftarrows Me_2C(OH)CN \xrightarrow{H_2O,\,MnO_2} Me_2C(OH)CONH_2, \\ \xrightarrow[MnO_2]{H_2O} Me_2C(NH_2)CONH_2 \xrightarrow{H_2O,\,MnO_2} Me_2C(NH_2)COOH + NH_3. \end{array} \right.$$

The replacement of α-aminoisobutyronitrile in the above system by its hydrochloride rules out hydrolysis almost completely and appreciably accelerates the hydration, which leads to a virtually quantiative yield of α-aminoisobutryamide hydrochloride (45 °C, 1 h). The subsequent binding of the hydrogen chloride by a strong base and an increase of the temperature of the reaction mixture to 90 °C make it possible to achieve with the same yield the hydrolysis of the resulting amide, catalysed by manganese(IV) oxide, to α-aminoisobutyric acid. 2-Amino-2-methylbutyramide and 2-amino-2-methylbutyric acid are formed analogously from 2-amino-2-methylbutyronitrile.[63]

Data on the kinetics and mechanism of the hydration of nitriles in the presence of manganese(IV) oxide are of interest. S-Shaped kinetic curves for the hydration of benzonitrile in the presence of MnO_2 and small amounts of water, the acceleration of the reaction by the preliminary treatment of the catalyst with benzonitrile, its retardation as a result of a similar treatment with water, and other kinetic features of the hydration reaction suggested that the first stage of the process is the formation of an intermediate complex of the nitrile with MnO_2, which is then subjected to nucleophilic attack by water.[83] It follows from the relations presented above between the rate of hydration and the polar properties of the substituents in the nitrile molecules that, in the hydration in the presence of an excess of water, the rate-limiting stage is the second.[63,67] Kinetic data have shown[63] that the complex of the nitrile with MnO_2 is then attacked by water from the bulk phase.

In the reactions of hydroxynitriles the hydroxy-group as well as the nitrile group can react with the catalyst surface, for example, via the formation of hydrogen bonds. Under the conditions of the hydration α-hydroxynitriles with a tertiary OH group, such interaction is probably the cause of the acceleration of the dehydrocyanation side reaction in the presence of manganese oxide, which was mentioned above.

In view of the appreciable electron-accepting capacity of the group $\alpha\text{-}\overset{+}{N}H_3$, it was to be expected that the hydration of α-ammonianitrile, like the hydrolysis of α-ammonia-amide, will proceed at a higher rate than the corresponding reactions of the α-amino-compounds. However, as shown above, this happens only in the case of the hydrolysis. The opposite behaviour in the hydration reaction can be attributed to the fact that the α-aminonitrile is adsorbed on the acid centres of the catalyst via the highly basic NH_2 groups; since both σ-bonds in the group $C{-}C{\equiv}N$ are colinear,[1] contact between the CN group in the adsorbed α-aminonitrile, whose position is to a large extent fixed, and the surface of the catalyst is hindered for geometrical reasons with a consequent retardation of its reaction with water. In the hydration of α-ammonianitrile adsorbed on the catalyst via the nitrile group such steric hindrance does not arise.

Depending on their position in the nitrile molecule, the same functional groups have exerted the opposite influence on the reactivity of the nitrile group. Whereas substituents in the α-position in the nitrile capable of interacting with the catalyst play a negative role in the hydration, the β-substituents accelerate the hydration as a result of their interaction with the catalyst. Presumably the higher reactivity of 3-aminocarbonyl- and 3-hydroxy-propionitriles compared with 3-methoxypropionitrile (see above) is due to the interaction of both the $CONH_2$ or OH group and the CN group with the surface of the catalyst, which leads to the formation of energetically favourable closed structures and to an increase of the surface concentration of the substrate.

It is striking that hydrocyanic acid is not hydrated in the presence of MnO_2 and is instead oxidised to cyanogen. This may be a consequence of the formation of the hydrogen bond between the hydrogen atom of HCN and the oxygen-containing groups on the surface of the catalyst with subsequent elimination of the hydrogen atom from the HCN molecule.[63]

Despite the fact that manganese(IV) oxide proved to be a highly active catalyst of the hydration of nitriles, in some cases its application is limited, as shown above, by its high oxidising capacity, as a result of which the addition of water to the nitrile group is not always the main pathway in the

reaction between reactants. Hydration in the presence of other metal oxides is therefore of interest.

Numerous oxides proposed as hydration catalysts are inactive or their activity is low[120] in the temperature range where hydration takes place in the presence of MnO_2. The study of the interaction of benzonitrile with water in the presence of various oxides under comparable conditions[84] showed that hydration proceeds at an appreciable rate as a rule only at 175–225 °C. Hydration is induced by almost all transition metal oxides, but, not counting MnO_2, the oxides of the iron subgroup elements proved to be the most active. Results of practical interest have been obtained with iron(III) oxide. At 225 °C benzamide has been obtained in 71% yield (the yield of benzoic acid was 7.5%); when Fe_2O_3 is re-used, its activity does not fall. In contrast to MnO_2, iron(III) oxide proved to be an extremely effective catalyst of the hydration of readily oxidisable nitriles such as phenylacetonitrile and diphenylacetonitrile. It has been shown that the hydration of nitriles in the presence of Fe_2O_3, as in the presence of MnO_2, is preceded by the interaction of the catalyst with the CN group.[84] Cobalt(III) and nickel(III) oxides are no less active in the hydration of benzonitrile than Fe_2O_3, but, under the conditions investigated (Co_2O_3 at 225 °C and Ni_2O_3 already at 175 °C), they interact to an appreciable extent with the reaction products, which rules out their reuse. After prolonged refluxing of aqueous solutions of 3- and 4-cyanopyridines in the presence of NiO, high yields of the amides were obtained.[33] On the other hand, in the reaction of 2-cyanopyridine under the same conditions, the amide obtained hydrolyses to 2-carboxypyridine, which forms a chelate compound with a catalyst. It has been suggested that the geminal positions of the nitrogen atoms of the pyridine ring and of the amide group of this compound are responsible for their simultaneous and specific adsorption on the same catalytic surface centre, which is the cause of the ready hydrolysability of the amide group.[33] At the same time the hydration of 2,4- and 2,6-dicyanopyridines to the corresponding dicarboxamides has been achieved in another study[38] in the presence of NiO.

In the hydration of benzonitrile (at 225 °C) copper(II) and zinc oxides proved to have activities similar to those of the oxides of the iron subgroup elements. However, in the presence of CuO the reaction products interact with the catalyst, while in the presence of ZnO the hydration is accompanied to a large extent by the hydrolysis of the benzamide formed.[84] Under milder conditions (refluxing of the aqueous solutions), copper(II) oxide proved to be a weak catalyst of the hydration of 3- and 4-cyanopyridines, but, like NiO, it induces appreciable hydrolysis of 2-cyanopyridine and the formation of a chelate compound.[33] Zinc oxides accelerates slightly the hydrolysis of stearonitrile at 180 °C.[85]

The analogues of zinc oxide in the subgroup, namely the cadmium and mercury(II) oxides, undergo irreversible changes in the course of the reaction.[84] It has been shown[86] that cadmium oxide is bound in the form of a salt to the benzoic acid formed. The interaction of benzonitrile and of *p*-substituted benzonitriles with water and CdO has been directed towards the formation of diamminecadmium benzoates in quantitative yields:

$$2RC_6H_4CN + 3H_2O + CdO \rightarrow (RC_6H_4COO)_2Cd\cdot 2NH_3.$$

The reactions catalysed by metal oxides are frequently catalysed also by the sulphides of the same metals. In the presence of copper(II) sulphide 25% of benzamide has been obtained from benzonitrile at 225 °C. The instability of CuS in the presence of water was also manifested under these conditions.[87]

The activity of the oxides of Group IIA elements proved to be low and approximately the same.[84] Among the oxides of Group III elements, alumina proved to be a weak but extremely selective hydration catalyst.[84] The adsorption of nitriles on this oxide is accompanied by their partial conversion into amides.[88,89] High yields of aromatic and saturated aliphatic amides have been obtained[90] on refluxing solutions of the corresponding nitriles in t-butyl alcohol in the presence of alumina modified by treatment with potassium fluoride.[91] The water required for hydration is present in the catalyst. Alumina and potassium fluoride taken separately do not induce an appreciable hydration of the nitriles, other conditions being equal.

Among the oxides of Group IV elements, a satisfactory yield of benzamide (59%) is obtained in the presence of lead(II) oxide. Zirconium and germanium(IV) oxides exhibit a weak catalytic activity, while titanium(IV) and silicon oxides are almost inactive. Among the oxides of Group V elements, a tendency has also been observed towards an increase of activity with increase of the atomic weight. In the presence of Bi_2O_3 and V_2O_5 benzamide has been obtained in almost identical satisfactory yields and both oxides also give rise to an appreciable hydrolysis of benzamide.[84] (The hydrolysis of amides in the presence of V_2O_5 at 150–180 °C has been used as a preparative method of synthesis of carboxylic acids.[92]) The activity of the oxides of Group VI metals increases in the sequence $Cr_2O_3 < MoO_3 < WO_3$. In the presence of the last oxide 41% of benzamide was obtained at 225 °C (with a selectivity of 95%).[87]

Comparison of the hydrating capacities of various higher and lower oxides of the same metals showed that in all cases the higher oxides are more active. A relation between the activities of various oxides and their acid–base properties has not been discovered. Thus the activities of Bi_2O_3 and V_2O_5, the first of which has basic properties and the second has acid properties, are similar.[84] Nor has it been possible to correlate the activities of various metal oxides with the electronic configurations of the corresponding cations. Overall, the oxides of transition metals with moderate acid–base properties proved to be the most active and selective in the reaction considered.

2. Hydration in the Presence of Metal-Containing Catalysts

Among the known metal-containing catalysts, the most active in the hydration of nitriles are those based on copper. It is known that metallic copper is a catalyst of the alkaline hydrolysis of polyacrylonitrile.[93] However, the first attempts at the hydration of nitriles in the presence of catalysts based on metallic copper were described subsequently.[33,94,95] The best results were achieved in the hydration of 2-, 3-, and 4-cyanopyridines in aqueous solutions: the yield of the amides reached 50% for a low selectivity. Later the first patent was published[96] on the hydration of acrylonitrile and other nitriles in the presence of catalysts incorporating, together with copper salts, which the authors erroneously assumed to be the main carriers of catalytic properties, also zerovalent copper. Since then numerous versions of copper catalysts for the hydration of nitriles (copper on oxide and organic polymeric carriers,[97] Raney copper, and powdered copper with a high surface area) have been described mainly in the patent literature.[2] The catalysts are obtained in the usual way, i.e. by reducing mixtures of finely dispersed copper(II) oxide and other oxides, for example the Atkins catalyst, prepared beforehand. Copper(II) oxide is usually reduced at 170–250 °C with hydrogen, the activity of the catalyst increasing with decrease of the hydrogen content in

its mixture with nitrogen or another inert gas.[98] At a reduction temperature of 210 °C the optimum hydrogen content in the hydrogen–nitrogen mixture is 3 mole %. The rate of hydration increases with increase of the degree of reduction of CuO, but the presence of small amounts of CuO and Cu_2O in the copper catalyst does not exert an appreciable influence on its activity.[99,100] The rate of hydration is influenced also by inorganic salts present as admixtures in the liquid component of the reaction mixture and in the catalyst.[121,122]

In order to obtain active copper powders, copper salts (sulphates, chlorides, acetates, etc.) are also reduced by metal hydrides, alkali metal tetrahydroborates, metals, hydrazine, formaldehyde, and other reductants.[2] As a rule, there is no direct relation between the activity of the catalysts and their surface area (10–120 $m^2\ g^{-1}$). The nature of the carrier has a greater influence on the activity.

After prolonged use in continuous processes, copper containing hydration catalysts are gradually deactivated, which is accounted for by the oxidation of copper by the traces of atmospheric oxygen dissolved in the reaction mixture and by the blocking of the catalyst surface by copper(II) oxide. The regeneration of oxide catalysts consists in their reduction, in the first place by hydrogen, as described above. Additional oxidation of the partly spent catalyst by atmospheric oxygen before its reduction may prove useful.

The efficiency of the regeneration of catalysts which have lost their activity depends to a large extent on the nature of the carrier. Thus the catalyst obtained by the thermolysis (in the presence of hydrogen) of copper formate deposited on the cross-linked copolymer of 4-vinylpyridine and 1,4-divinylbenzene contains finely dispersed copper and exhibits a high initial activity in the hydration reaction.[97] However, after its deactivation, it is impossible to restore fully its activity by passing hydrogen, while less dispersed copper catalysts obtained under the same conditions on metal oxides are readily regenerated. It has been suggested[97] that the finely dispersed copper on the polymeric carrier becomes partially aggregated on contact with atmospheric oxygen. It is also possible that the carrier undergoes chemical changes in the course of the high temperature reduction and this is responsible for the alteration of its influence on the activity of copper.

One of the ways of increasing the lifetime of copper-containing catalysts involves the introduction of halide ions into the reaction mixture,[101] in particular of potassium bromide.[102] The catalytic activity of the oxidised copper is almost fully restored after it has been treated with potassium iodide.[103]

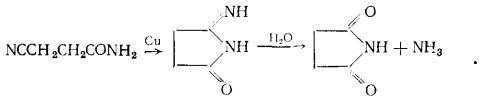
Aromatic and unsubstituted aliphatic nitriles are hydrated with a high selectivity in the presence of various copper-containing catalysts; appreciable amounts of side products have not been detected. The yields of aliphatic amides at 100–110 °C are close to theoretical values.[104] The synthesis of benzamides with a substituted amino-group in the 2-position from 2-chlorobenzonitrile and piperidine or another cyclic base in the presence of a bronze is apparently based on the hydration of aromatic nitriles in the presence of copper.[105]

The kinetics of the hydration of aromatic nitriles for a molar ratio of water and the nitrile of 1.5 : 1 in dioxan in the presence of the Cu–MgO catalyst are described by a second-order equation. The effective specific rate constants for the hydration increase with increase of the electron-accepting capacity of the substituent in the benzene ring of the nitrile. A satisfactory correlation has been established between these constants and the Hammett σ constants (ρ = +0.33).[104] The kinetics of the hydration of aliphatic nitriles in an excess of water in the presence of the Cu–MgO catalyst obey a first-order equation. A satisfactory correlation between the effective specific rate constants and the Taft σ^* constants (ρ = +1.78) has been observed for the hydration of acetonitrile, propionitrile, butyronitrile, 3-hydroxypropionitrile, and acrylonitrile. The low absolute reaction constants show that the polarity of the transition state in the hydration of nitriles in the presence of copper catalysts is low.[104]

In the presence of the Cu–MgO catalyst chloroacetonitrile partly undergoes side reactions with evolution of hydrogen chloride, which interacts with the catalyst. On lowering the hydration temperature to room temperature, it was possible to suppress to a large extent the formation of HCl and to obtain a high yield of chloroacetamide. In the presence of this catalyst 3-chloropropionitrile undergoes dehydrochlorination together with hydration, which leads to the formation of acrylamide as the main reaction product.[104]

In contrast to 2-hydroxynitriles, 3-hydroxypropionitrile is hydrated smoothly in the presence of copper (activation energy E_a = 60 kJ mol^{-1} at 90–110 °C).[104,106] 2-Methoxyisobutyronitrile is also hydrated, although the reaction is very slow owing to steric hindrance.[107]

The hydration of the nitriles of dibasic aliphatic acids in an excess of water in the presence of the Cu–ZnO–Al_2O_3 catalyst has been described.[68] Adiponitrile is hydrated, as in the presence of manganese(IV) oxide, initially to 5-cyanovaleramide, which is then converted into adipamide. The hydration of succinonitrile involves the formation of 3-cyanopropionamide and succinimide (instead of succinamide as in the presence of MnO_2). Malononitrile is hydrated to 2-cyanoacetamide and at the same time is partly converted into a polymeric product. In the presence of an excess of water the ratios of the rate constants for the addition of the first water molecule to adipo-, succino-, and malono-nitriles are 1.35 : 1 : 9. The highest reactivity of malononitrile can be naturally accounted for by the mutual activation of the two cyano-groups. However, the lower rate constant for succinonitrile than in the hydration of adiponitrile is unexpected, since the negative polar effect of the 2-cyanoethyl group of succinonitrile is somewhat greater than that of the 4-cyanobutyl group of adiponitrile. Presumably the hydration of succinonitrile is preceded by the interaction of the active centres of the catalyst, in close proximity, with both cyano-groups of the dinitrile with formation of a cyclic complex, in which at least one cyano-group is π-bonded to the metal. On the other hand, in the hydration of adiponitrile such a cyclic complex would be strained and in this case electron-donating properties are therefore shown only by the *n* electrons of the cyano-group, which is the reason for the higher reactivity of adiponitrile. The unusual interaction of succinic acid derivatives with the copper catalyst may be responsible also for the fact that 3-cyanopropionamide is not hydrated but undergoes cyclisation in an aqueous solution in the presence of zerovalent copper:



It is noteworthy that the rate constant for the hydration of adiponitrile is greater by a factor of ~1.7 than for 5-cyanovaleramide.[68] A greater reactivity of the cyano-group in the adiponitrile molecule than in the compound where one cyano-group has already reacted has been observed also in a number of other reactions of adiponitrile.[1]

The hydration of acrylonitrile in the presence of copper-containing catalysts has been studied more thoroughly than for any other nitrile. The numerous varieties of catalysts based on zerovalent copper described have been proposed primarily for the hydration of acrylonitrile. In the presence

of copper-containing catalysts acrylamide is formed in high yields. In the presence of the $Cu-Cr_2O_3$ catalyst at temperatures not exceeding 120 °C up to 90% of acrylonitrile is converted into acrylamide when the catalyst is used repeatedly.[108] The Cu–MgO and $Cu-ZnO-Al_2O_3$ catalysts as well as Raney copper also exhibit a high activity in the hydration of acrylonitrile.[97,108,109] After prolonged hydration in the presence of the $Cu-SiO_2-MgO$ catalyst, the yield of acrylamide is 85%.[97] Certain technological aspects of the hydration of acrylonitrile in the presence of $Cu-ZnO-Al_2O_3$ in an excess of water and, in particular, the quantitative dependence of the rate of hydration in a continuous process on temperature, the linear flow rate in the reactor, and the initial concentration of acrylonitrile in the reaction mixture, as well as the phase equilibria in the systems formed by the initial nitrile, the amide, water, and other substances have been examined.[71,108,110,111] The hydration of acrylonitrile in the presence of Raney copper in a flow-circulation system has been described[112] and the same paper also presents an empirical equation for the process kinetics.

The hydration of acrylonitrile in the presence of copper-containing catalysts is not fully regioselective. Together with the hydration of the cyano-group, water adds to the C=C bond under the reaction conditions with formation of 3-hydroxypropionitrile, which then partially reacts with a second acrylonitrile molecule or undergoes hydration. This leads to the formation of di(2-cyanoethyl) ether and 3-hydroxypropionamide.[106] These reactions have been studied quantitatively in the hydration reaction in the presence of the $Cu-ZnO-Al_2O_3$ catalyst.[106] It has been found that, by virtue of their occurrence in the temperature range 80–120 °C, the selectivity of the hydration to acrylamide is 97–93%. At 100 °C in a continuous process the selectivity increases to 99.5% (for a degree of conversion of acrylonitrile of 90%) as a consequence of the elution from the catalyst of traces of alkali, which catalyse the addition of water to the C=C bond. The hydration of the double bonds is also accelerated by copper(II) oxide, which is incorporated to a greater or lesser extent in the catalysts based on metallic copper.[123] However, the possibility of the side reaction involving the formation of 3-hydroxypropionitrile depends not only on the admixture in the catalyst but also on the structure of the latter. Whereas in the hydration reaction in the presence of Raney copper carefully washed with water acrylamide is virtually the only reaction product, when catalysts deposited on certain carriers are employed 3-hydroxypropionitrile is formed in appreciable amounts; under these conditions, the more basic the carrier the lower the selectivity of the hydration to acrylamide (for example, water adds to the C=C bond particularly vigorously in the presence of the Cu–MgO catalyst).[71,97] The replacement of the basic MgO by the SiO_2-MgO carrier, which exhibits acidic properties, made it possible to suppress to a large extent the formation of 3-hydroxypropionitrile: under comparable conditions in the preparation of the catalysts and their tests, the selectivity in the formation of acrylamide increased from 75% to 97%.[97] It is therefore undesirable to employ catalysts containing basic components for the hydration of the C≡N group in unsaturated nitriles capable of combining with water via the C=C double bond, although these catalysts may be entirely suitable for the synthesis of amides from other nitriles.

Small amounts of other side products are also formed in the hydration of acrylonitrile. Thus traces of acrylamide hydrolysis products, namely, acrylic acid and ammonia, have been found in the reaction mixture.[106,113] Only above 120 °C are these admixtures formed in more appreciable amounts.[108] Microadmixtures of a number of unsaturated amides, namely heptatrienamide, pentadienamide, and 5-cyanopent-2-enamide, which may be the products of the catalytic hydration of the corresponding nitriles present as admixtures in the initial acrylonitrile, have been detected in acrylamide.[114] Under the conditions of the hydration reaction in the presence of Raney copper containing adsorbed hydrogen, there is a possibility of side reactions involving the hydrogenation of acrylonitrile, which leads to the appearance of admixtures of n-propylamine in acrylamide.[2]

The kinetics in the initial period of the hydration of acrylonitrile in an excess of water are described by an equation which is of first order with respect to the nitrile ($E_a = 75.8–86.7$ kJ mol^{-1}).[100,108] In an excess of acrylonitrile the reaction is also of first order with respect to water.[100] In the hydration of acrylonitrile as well as other nitriles in an excess of water up to high degrees of conversion the reaction kinetics do not obey the equation derived for the initial period of the hydration process, which can be explained by the inhibition of the reaction by the amides formed, through preferential adsorption of acrylamide on the catalyst surface.[71,97,100,109,122] Calculation based on the kinetic data for high degrees of conversion using different copper catalysts on carriers[97] showed that the ratios of the adsorption coefficients for a number of amides and the corresponding nitriles are 10 : 1–50 : 1. It has been shown recently that acrylamide is not the only reaction product inhibiting the hydration of acrylonitrile. The acrylic acid formed in the hydrolysis of acrylamide in an amount as much as 0.7 mole % of the initial nitrile reduces the rate of hydration under comparable conditions by more than a factor of two. Under the influence of acrylamide, the same effect is attained when its content is ~15%. Another side product, namely 3-hydroxypropionitrile, does not affect the rate of hydration of acrylonitrile.[100]

Under conditions of the hydration of methacrylonitrile in the presence of copper-containing catalysts, side reactions do not occur to an appreciable extent, in contrast to acrylonitrile; methacrylamide (96%), which is an industrial monomer, and the nitrile which has failed to react have been isolated from the reaction products. The first order reaction rate constant diminishes during hydration with increase of the content of the amide in the reaction mixture. The activation energy in the temperature range 61–90 °C is 55.7 kJ mol^{-1}.[115]

Raney copper has been used as the catalyst of the hydration of the cyano-groups of polyacrylonitrile in a saturated aqueous solution of potassium thiocyanate. A polymer containing up to 34% of acrylamide elementary units was obtained. Polymerisation via the cyano-groups with formation of azapolyene sections in the macromolecules also occurs under the hydration conditions.[71,72]

The data for the hydration of nitriles in the presence of oxide catalysts (see above) suggest that the hydration in the presence of copper includes a stage in which the nitrile interacts with the catalyst (activation of the cyano-group) with subsequent addition of water. The data presented above for the kinetics of the hydration of dinitriles[68] agree with the hypothesis that the cyano-group interacts with the catalyst surface. Important evidence in support of this is provided by the polymerisation via the cyano-groups of polyacrylonitrile under the influence of a hydration catalyst, i.e. the occurrence on copper of a reaction in which water is not involved. The positive reaction constants ρ in the Hammett and Taft equations presented above show that the rate of hydration of nitriles is limited by the rate of nucleophilic attack by water on the CN group.[104] If the interaction of the catalyst with the nitrile, for example the formation of a complex, were the rate-limiting stage, then the constant ρ would have had the opposite sign. The mechanism proposed by Elsemongy and Onsager,[109] according to which the catalyst

activates both the nitrile and water, is also inconsistent with the observed correlations. Thus the sequence of the principal stages of the hydration process is apparently clear. However, it has been shown[100] that, in order to refine the reaction mechanism, it is necessary to carry out additional studies on the adsorption and other processes occurring during hydration.

An attempt has been made to hydrate the thiocyanate group in organic compounds in the presence of a copper catalyst.[116] However, when an aqueous solution of methyl thiocyanate was heated in the presence of Raney copper, only insignificant amounts of *S*-methyl thiocarbamate were found in the reaction products. It was discovered that the main reactions of methyl thiocyanate involve the hydrolysis of the SCN and $SCONH_2$ groups at the sulphur–carbon bond and the homolytic reactions of the SCN group induced by the presence of copper.

Catalysts based on metallic nickel have also been used for the hydration of nitriles.[33,94,95,117] Urushibara nickel (nickel on a zinc carrier) and Raney nickel proved to be the best catalysts. The hydration was carried out by prolonged refluxing of nitriles with an excess of water in the presence of these catalysts. The amides have been obtained in high yields from benzonitrile, a series of *p*-substituted benzonitriles, and 3-, 4-, and 2-cyanopyridines. *o*-Substituted benzonitriles and aliphatic nitriles have been converted into amides in moderate yields. The hydration of nitriles entails the simultaneous formation of acids and amines (the latter evidently as a consequence of the hydrogenation by the hydrogen adsorbed on the catalyst). The hydration of amino- and nitro-benzonitriles is accompanied by side reactions of the resulting amides with the catalyst. Only nickel and zinc complexes have been obtained in the case of *p*-hydroxy- and *o*- and *p*-cyano-benzonitriles, *p*-cyanobenzoic acid, ethyl *p*-cyanobenzoate, and *p*-cyanobenzaldehyde. The introduction of pyridine into the reaction mixture increases the yield of the amides, while the introduction of thiophen and organic acids lowers their yield. It has been suggested[95] that the hydration is preceded by the adsorption of the cyano-groups on nickel, mainly on its basic centres.

The studies of the hydration reaction in the presence of the nickel catalysts examined above were carried out in the 1960's. In view of major practical advances achieved in the employment of copper as a hydration catalyst, subsequently nickel catalysts attracted little attention.[55]

Among other metallic catalysts, mention has been made of "activated iron"[55] and iron–zinc[2] and platinum[1] catalysts.

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Thus the present review shows that the advances in various new aspects of the hydration of nitriles are not all of equal value. Significant results have been obtained in the homogeneous hydration of coordinated nitriles. It has been established that coordination is responsible for a very considerable increase of the rate of hydration (by a factor up to $\sim 10^{18}$). Considerable experimental data have now accumulated on the synthesis in these reactions of amides (coordinated to different ions) in high yields. In a number of instances the study of the hydration kinetics made it possible to examine in detail the reaction mechanism and to put forward entirely feasible mechanisms for the reactions of the initial complexes. It has also been found that the coordinated nitriles also enter into other reactions in aqueous solutions, the latter being determined by the structure of the nitriles and sometimes by the reaction conditions. At the same time there have been no systematic studies of the hydration of a sufficiently wide range of nitriles and of the influence of the structure of the initial complexes on the characteristic features of the hydration process. The preparative value of the hydration reaction under consideration is as a rule limited, because the isolation of the free amides requires the chemical modification or even the decomposition of the amide-containing complexes obtained.

The homogeneous-catalytic hydration of nitriles in the presence of complexes as catalysts, which leads to the formation of amides not linked chemically to the complexes present in the reaction mixture, has so far been comparatively little studied. There have been as yet no kinetic investigations of the reaction and high rates of hydration and degrees of conversion approaching quantitative values have not been achieved. However, the proposed fundamental mechanism of the catalytic action of complexes appears to be correct. Apparently the main task in this field is the choice of new catalytically more active complexes and the develoment of conditions for the isolation of the amides formed, which will make it possible to increase the preparative values of the method.

The best practical results have so far been achieved in the heterogeneous-catalytic hydration of nitriles. This hydration method has undoubted advantages over other considered in this review and also those described previously[1] in view of its simplicity, high yields of the amides, and also because reactants other than nitriles are hardly consumed in the synthesis of the amides. All these factors have served as a basis for the employment of heterogeneous-catalytic hydration of nitriles in industrial organic synthesis. During the last 5–10 years, studies have been made of the kinetics and mechanism of the hydration reaction and many of its features in the presence of manganese(IV) oxide and copper-containing and other catalysts have become understood, which made it possible to propose reliable reaction mechanisms, but these require a certain amount of experimental confirmation and specification in greater detail. In view of the similarity of the characteristics of the hydration of certain substituted nitriles under the conditions of heterogeneous catalysis and in a homogeneous medium containing complexes with the same nitriles as ligands and also in view of the weak dependence of the activation energies for the hydration of nitriles on the method of hydration, it is to be expected that the achievements in the study of the mechanism of homogeneous hydration will promote the solution of urgent problems in the heterogeneous-catalytic hydration of nitriles.

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Zhdanov Gorky Polytechnic Institute

Translated from *Uspekhi Khimii*, 53, 1572-1594 (1984) U.D.C. 543.544.25

The Development of Circulation Gas Chromatography

M.P.Zabokritskii, V.P.Chizhkov, and B.A.Rudenko

The present state of circulation gas chromatography, and its principal regular features and apparatus, have been examined. A highly effective version of circulation gas chromatography has been proposed. It has been shown possible to achieve a high efficiency in the separation of organic compounds with similar structures and properties (several tens of thousands of theoretical plates with a specimen of up to 1 g).
The bibliography contains 159 references.

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I. INTRODUCTION

In recent years, as a result of the intensified study in the field of present-day organic chemistry, it has become necessary to carry out the fine preparative separation of organic compounds showing extremely small differences in their structures and properties (for example, similar structural and spatial isomers). Attempts to solve this problem using the classical methods encountered in laboratory practice (distillation, extraction, crystallisation, etc.) do not always give the desired results. Moreover, the restricted nature of the possibilities provided by these methods becomes increasingly apparent with the increased complexity of the task of fine preparative separation. The difficulty of separating isomers is also increased by the fact that newly synthesised organic compounds are often available only in very small quantities. At the same time, the extremely marked differences in the chemical properties and biological activities of a number of isomeric molecules make the problem of their separation and individual study extremely important.

The present-day level of gas-chromatographic procedures and techniques makes it possible to separate substances with extremely similar structures and properties. In most cases, however, chromatographic methods, which have a high efficiency of separation, have an extremely low productivity, making it possible to work only with specimens with masses of 10^{-3}–10^{-6} g. These systems — capillary columns, very long (up to 100 m) packed columns with a small diameter, and short packed columns included in a circulation scheme — are used successfully to separate multicomponent mixtures, similar structural and spatial isomers, and isotopes and isotopically substituted compounds. The efficiency of the preparative separation of specimens of a mixture of substances, however, even in amounts corresponding to several tenths of a gram, is usually much lower, and rarely exceeds 3–5 thousand theoretical plates (t.p.). At the present time, in gas chromatography, the only methodological version making it possible to separate gram quantities of substances with an efficiency of about 30–50 thousand t.p. is apparently preparative circulation chromatography.

Since the publication of the first reviews of circulation gas[1] and liquid[2] chromatography, new papers have been published, developing the theory and extending the range of application of this method.

The present review examines chiefly development circulation gas chromatography (CGC), which is not, however, the only method of circulation separation. Versions of the circulation method have found application in heat-dynamic gas,[3] liquid,[4-29] and thin-layer[30] forms of chromatography. The preparative separation of a number of substances has been described.[31-34] Capillary circulation chromatography appears promising for some cases of extremely fine separation.[35,36]

II. VERSIONS OF THE CIRCULATION METHOD AND APPARATUS

The idea of circulating the specimen to be separated in a closed cycle with a layer of sorbent, suggested by Martin,[37,38] found practical application in two different types of technical apparatus. In the first case, the circulation of the specimen and the mobile phase is carried out in a single cycle by the action of a circulating pump. In the second version, recirculation of the mobile phase does not take place, and the circulation of the band of compounds being separated is brought about by a periodic change in the direction of the gas stream by means of special tap or valve switching devices.

In 1959–1960, Porter and Johnson[39-41] described the first circulation apparatus consisting of a closed circuit with two chromatographic columns, detector, input device, and peristaltic circulation pump. A similar apparatus, differing only in the replacement of the peristaltic pump by a piston pump, was later used.[42,43] With apparatus of this type, considerable broadening of the chromatographic peaks was observed, because of the mixing action of the pump and the large dead volumes in the closed system, and this made it impossible to obtain a high efficiency of separation. Moreover, the temperature range of operation of these circulation pumps was found to be extremely restricted.

In the period 1960–1970, circulation apparatus with a periodic action and switching devices appeared,[44-50] in which the band of chromatographic compounds circulated without passing through the pump. This made it possible to increase the efficiency of the separation. The turning of the taps, however, leads to marked pneumatic disturbance, associated with the redistribution of the pressures in the column. This leads to additional broadening of the chromatographic band, and a large number of cycles cannot be carried out. In a

comparison of the two systems described, preference was given[49] to the circulation scheme with a pump in the main cycle.

Circulation chromatography developed considerably by the use of gas stream switching devices in various circulation schemes with a semi-continuous or continuous action, designed mainly for preparative and industrial chromatography. Among the semi-continuous systems, mention may be made of an apparatus in which portions of the mixture to be separated are introduced in each half-cycle into the middle section of the circulation band, and the separated products are removed by cutting off the end sections of the chromatographic zones of each component.[51,52] Systems with a continuous action include circulation apparatus in which the specimen is introduced by the alternate opening and closing of taps arranged round the circumference of a toroidal column, with stationary columns,[53-55] and apparatus in which the supply section remains stationary as a result of the rotation or reciprocating movement of the columns.[56-62] These versions of toroidal circulating assemblies can also operate under periodic conditions.[63,64] Circulation assemblies based on the use of frontal chromatography have also been developed.[65-67] Although they have a high productivity, these assemblies have not solved the problem of the highly effective preparative separation of similar structural and spatial isomers or isotopically substituted compounds, which represents the most difficult problem for the organic chemist and technical engineer.

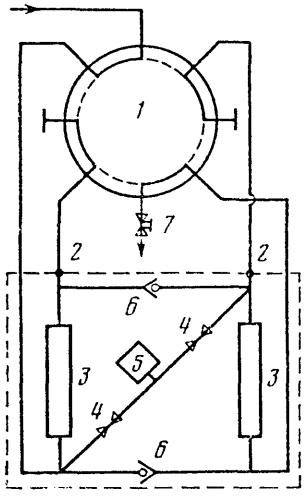


Figure 1. Circulation apparatus with unheated switching device: *1*) circulation tap, *2*) input devices, *3*) chromatographic columns, *4*) pneumatic resistance, *5*) detector, *6*) stream chopper valves, *7*) valve.

An unsatisfactory feature of many circulation schemes with gas stream switching devices is that the mixture being separated passes through the channels of the switching taps or valves. This makes it necessary to heat the switching assemblies, and this decreases their reliability of operation and the temperature range of application of the method, increases the dead gas volumes, and prevents the elimination of possible degradation of heat-sensitive compounds when they come into contact with the heated metal surfaces. In these schemes it is difficult to use pieces of apparatus made of glass.

To overcome these disadvantages, circulation schemes in which the switching tap is brought out of the thermostat have been proposed. In this case, the temperature restrictions are determined only by the thermal stability of the stationary liquid phase. The removal of the switching tap from the circulation circuit, however, led to considerable non-productive losses of the carrier gas and the substances being separated; these were lost to the atmosphere through the chokes connecting the column inlets and outlets,[68-70] or through auxiliary columns with a high resistance to the gas stream.[71,72] Further progress in CGC was achieved by using check valves or gate valves with a forced action to divide the gas stream,[73-75] replacing the economically unsuitable chokes. One possible form of circulation scheme with removal of the switching tap from the heated zone is shown in Fig.1.

The development of the circulation method of separation has been reflected in a number of Soviet (LKhP-4, LKhP-71, LKhM-9) and imported instruments. The universal attachments, developed by the Special Design Office of the Institute of Organic Chemistry of the Academy of Sciences of the USSR, with manual control or with programming and automatic switching of the circulation tap, PTsU-1 and PTsU-2, and attachments for chromatography in water vapour and for switching columns, P-1 and P-2, have made it possible readily to combine various versions of a circulation scheme with analytical and preparative gas chromatographs, for example LKhM-8MD, LKhP-51, etc. A specialised capillary circulation gas chromatograph, Biokhrom-27, is being developed at present (Special Design Office, Institute of Organic Chemistry of the Academy of Sciences of the USSR).

III. PRINCIPAL THEORETICAL REGULAR FEATURES OF CIRCULATION GAS CHROMATOGRAPHY

1. Dependence of the Efficiency of Separation on the Number of Chromatographic Cycles Carried Out

Early theoretical studies of the dependence of the efficiency of separation on the number of cycles carried out in the circulation scheme assumed a linear increase in the number of theoretical plates with increase in the number of columns through which the specimen passed.[47,76,77] Experiments showed, however, that the rate of increase in the efficiency of the separation usually decreases with increase in the number of columns passed through. A similar decrease in efficiency was noted in Ref.49. Sakodynskii and co-workers[32,78,79] observed a considerable fall-off in the increase in efficiency with increased number of cycles in a circulation preparative assembly; to make fuller use of the possibilities provided by the circulation scheme, the end zones of the peaks were removed without waiting for their complete separation.

A similar fall-off in the rate of the increase in the efficiency of separation with each new cycle was demonstrated in Refs.80 and 81. The observed effect was attributed to the influence of non-stationary regions in the gas stream, produced when the circulation tap was turned. As a result of the sharp redistribution of pressure in the columns when the tap is turned, part of the specimen in the gas phase is rapidly compressed, and moves forward relative to that part of the specimen present in the sorbed state in the stationary phase; for a finite rate of mass transfer, this leads to additional broadening of the chromatographic band.

Under the conditions described above, it was found appropriate to use long columns (10 m or longer),[33] which make it possible to reduce the number of times the circulation tap is turned and hence to decrease the rate of broadening of the chromatographic bands of the compounds being separated throughout the entire length of the column. Similar considerations apparently led other workers[82-85] to use columns with a length of 8–15 m for the separation of isotopically substituted compounds.

The limitations in the efficiency of separation attainable using circulation chromatography, which appeared at this stage of its development, produced in some workers a certain scepticism,[86] which was overcome only after an extensive analysis of the effects of pulse contraction and broadening of the chromatographic zones.

2. Effect of Pulse Contraction of the Chromatographic Zone

The effect of pulse contraction[88-90] of the chromatographic zone received its name by analogy with the pulse thermal enrichment[87] of the chromatographic zone. The essential features of this effect are as follows. If in the first chromatographic column of the circulation scheme through which the carrier gas moves, the linear velocity of the mobile phase is greater than that in the second column (as a consequence of the presence of the stream divider), then in the first column the trailing edge of the zone after a time t passes through a distance

$$l_1 = tu_1/(1 + k')$$

and the leading edge of the zone in the second column after the same time t passes through a distance

$$l_2 = tu_2/(1 + k')$$

where u_1 and u_2 are the linear velocities of the carrier gas in the first and second columns, and k' the extraction coefficient. As a result of the removal of part of the carrier gas between the columns, $u_1 > u_2$, that is $l_1 > l_2$. Thus the transfer of the band from one column to the other is accompanied by a contraction of the chromatographic zone in the ratio

$$b = l_2/l_1 = u_2/u_1 = 1 - a/100$$

where a is the mass fraction of the carrier gas removed between columns 1 and 2, expressed as a percentage. Thus the turning of the circulation tap will lead to a contraction of the chromatographic zone.

For columns consisting of a large number of identical sections, the width of the peak ν_m, the distance between the maxima of the peaks Δn_m, and the degree of separation R_m alter with change in the number m of columns passed through, as follows:

$$\nu_m = \nu_1 (m)^{1/2} \quad (1)$$

$$\Delta n_m = \Delta n_1 \cdot m \quad (2)$$

$$R_m = R_1 (m)^{1/2} \quad (3)$$

where ν_1, Δn_1, and R_1 are the parameters of the chromatographic band after its passage through the first column. Eqns.(1)–(3) describe the linear increase in the efficiency of separation with increase in the number of columns passed through.

Under pulse conditions, the width of the zone at the start of the second column is $\nu_1^0 = b\nu_1$. As a result of the broadening of the zone on passage through the second column, the width will be

$$\nu_2 = (b^2 + 1)^{1/2} \nu_1$$

After the transfer of the zone to the third column, the width of the band is reduced to

$$\nu_2^0 = (b^4 + b^2)^{1/2} \nu_1$$

after which it increases to the following value:

$$\nu_3 = (b^4 + b^2 + 1)^{1/2} \nu_1$$

As a result of the alternate contraction and broadening of the band, the width of the chromatographic zone after passage through m colums will be

$$\nu_m = [b^{2(m-1)} + b^{2(m-2)} + \ldots + b^2 + 1]^{1/2} \nu_1 = \left(\frac{1 - b^{2m}}{1 - b^2}\right)^{1/2} \nu_1 \quad (4)$$

Thus the broadening of the zone of a chromatographic compound in the circulation zone with removal of some of the gas between the columns is less than that given by Eqn.(1). The increase in the width of the zone is restricted to the limit

$$\nu_\infty = (1 - b^2)^{-1/2} \nu_1$$

reached as $m \to \infty$.

Similar arguments can be used to examine the change in the distance between the maxima of the bands of two chromatographic compounds. After the zone has passed through m columns, the distance between the maxima of the bands will be:

$$\Delta n_m = \frac{1 - b^m}{1 - b} \cdot \Delta n_1 \quad (5)$$

From this equation it follows that in a circulation scheme with removal of gas, the increase in Δn_m is less than that expected from Eqn.(2). The value of Δn_m as $m \to \infty$ will be

$$\Delta n_\infty = \frac{1}{1 - b} \cdot \Delta n_1$$

that is the distance between the band maxima in a circulation scheme with removal of gas is restricted to a certain limiting value.

Eqns.(4) and (5) give

$$R_m = \left(\frac{1 + b}{1 - b} \cdot \frac{1 - b^m}{1 + b^m}\right)^{1/2} R_1 \quad (6)$$

It follows from Eqn.(6) that the increase in the degree of separation is also restricted to the limiting value:

$$R_\infty = \left(\frac{1 + b}{1 - b}\right)^{1/2} R_1$$

The theoretical ideas about pulse chromatographic conditions were verified experimentally[89] using a model mixture of benzene and cyclohexane. The relationships obtained are given in Fig.2. When part of the gas stream is removed, the chromatographic zone eventually reaches an equilibrium state in which there is practically no further broadening of the zone, and simultaneously no further change in the values of ν_m, Δn_m, and R_m. The lack of agreement between the experimental curves and the curves corresponding to the theoretical equations (4), (5), and (6) is attributed to the effect of the pulse broadening of the zone.

3. Effect of Pulse Broadening of the Chromatographic Zone

The effect of pulse broadening of the chromatographic zone[90,91] is the opposite of the effect examined above, and is due to the existence of a gradient in the linear velocity of the carrier gas in the columns of the circulation scheme.

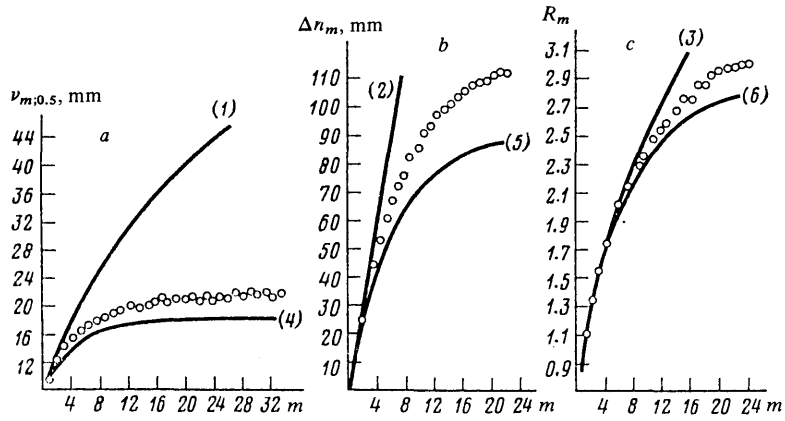


Figure 2. Dependence of the peak width at half-height $\nu_{m;0.5}$ (*a*), the distance between the maxima of the peaks Δn_m (*b*), and the degree of separation R_m (*c*) on the number of half-cycles m; the numbering of the curves corresponds to the numbering of the equations, and the points correspond to the experimental data. Conditions: two 4 m × 4 mm columns containing 5% Apiezon L, inlet pressures p_{in} = 1.1 MPa, outlet pressure p_{out} = 1.0 MPa, gas removal kept at a level of 12–13%.

The essential features of this effect are as follows. When there is no removal of gas between the columns, the linear velocity of the carrier gas in the columns increases continuously. The leading edge of the zone will move in the second column at an average velocity which is greater than that of the trailing edge remaining in the first column. The difference in the rates of movement of the edges of the zone, combined with the subsequent pulse redistribution of the velocities, will lead in each half-cycle to additional broadening of the bands of the chromatographic compounds, which increases from one cycle to another. Thus the movement of the chromatographic zone through the entire length of the column of the circulation scheme will take place slightly earlier than indicated by Eqns.(1) and (2).

The changes in the principal chromatographic characteristics with variation of the number m of columns passed through, with allowance for the effect of pulse broadening of the chromatographic zone, are given by the following equations:

$$b_0 = \bar{u}_2/\bar{u}_1$$

$$\nu_m = \left(\frac{b_0^{2m}-1}{b_0^2-1}\right)^{1/2} \nu_1 \qquad (7)$$

$$\Delta n_m = \frac{b_0^m - 1}{b_0 - 1} \cdot \Delta n_1 \qquad (8)$$

$$R_m = \left(\frac{b_0+1}{b_0-1} \cdot \frac{b_0^m-1}{b_0^m+1}\right)^{1/2} R_1 \qquad (9)$$

Here, b_0 is the zone broadening factor for the chromatographic compounds ($b_0 > 1$), and u_1 and u_2 the average linear velocities of the carrier gas in the first and second columns along the path of the gas.

According to Eqn.(9), the increase in R_m is restricted to the limiting value:

$$R_\infty = \left(\frac{b_0+1}{b_0-1}\right)^{1/2} R_1$$

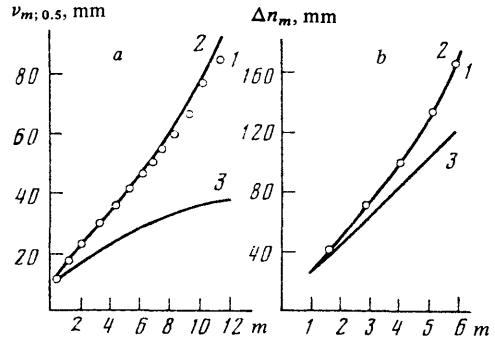


Figure 3. Dependence of the peak width at half-height $\nu_{m;0.5}$ (*a*) and the distance between the maxima of the peaks Δn_m (*b*) on the number of half-cycles m; *1*) experimental points; *2* and *3*) theoretical curves corresponding to Eqns. (7), (8) and (1), (2) respectively. Conditions: two 3 m × 4 mm columns containing 20% Apiezon L, p_{in} = 0.57 MPa, C = 1.24, no removal of gas.

The factor b_0 depends on the ratio C of the pressure at the inlet to the pressure at the outlet of the circulation assembly. For $C \leq 1.4$, it may be assumed that

$$\bar{u}_1 = (u_{out}/C + u_{1/2})/2$$
$$\bar{u}_2 = (u_{out} + u_{1/2})/2$$
$$u_{out}/u_{1/2} = [(C^2+1)/2]^{1/2}$$

where $u_{1/2}$ is the local linear velocity of the carrier gas at the outlet from the first column in the path of the gas. Thus b_0 is given by the expression

$$b_0 = \frac{[(C^2+1)/2]^{1/2}+1}{[(C^2+1)/2]^{1/2} \cdot \frac{1}{C}+1} \approx C^{1/2}$$

It follows from this equation that a decrease in C (for a constant pressure drop) leads to a decrease in the influence of the pulse effect in broadening the chromatographic zone. This conclusion has been confirmed experimentally.[92–95]

The dynamics of the change in the chromatographic parameters were studied using a circulation assembly with an eight-way tap in a scheme with two columns. The materials studied were the same as in the first case. Fig.3 shows that the above theoretical ideas about the pulse effect in broadening the chromatographic zone are confirmed qualitatively and quantitatively by the experiments. Only six half-cycles could be carried out without cutting off components.

Fig.4 gives the experimental dependence of the number of theoretical plates n on the number of half-cycles m under conditions of different ratios of the inlet and outlet pressures with no removal of gas between the columns (curves *1* and *2*).

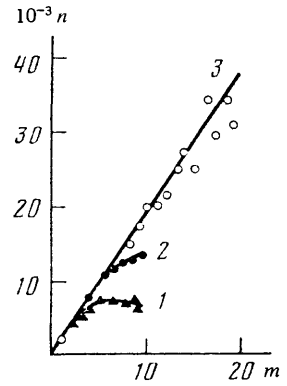


Figure 4. Dependence of the number of theoretical plates n on the number of half-cycles m: *1*) curve obtained at $C = 1.24$ (without gas removal) under the conditions described in Fig.2; *2*) curve obtained at $C = 1.06$ (without gas removal) under the following conditions: $p_{in} = 0.99$ MPa; *3*) straight line obtained under non-pulse chromatographic conditions for $C = 1.24$ ($a = 9.1\%$) at $p_{in} = 0.57$ MPa.

4. Non-pulse Circulation Gas Chromatography

The effect of pulse broadening of the chromatographic zone can be eliminated completely by compensating it by the effect of pulse contraction. This gives the optimum conditions of "non-pulse chromatography".†[90,91,96]

The optimum value, required to create these conditions, of the gas removal factor between the columns of the circulation scheme a can be estimated approximately from the material balance equation

$$S_1 u_1 d_1 = S_2 (u_2 d_2 + a u_1 d_1)$$

where S_1 and S_2 are the areas of the cross-section of the columns, occupied by the gas in the first and second columns of the circulation system, and d_1 and d_2 the densities of the gas in the chosen sections. When the sections of the columns are equal at points situated in the middle of the length of the columns, the following relationship will be observed:

$$a = 1 - u_2 d_2 / u_1 d_1$$

For non-pulse chromatographic conditions, $u_1 = u_2$, so that

$$a_{opt} = 1 - d_2/d_1 = 1 - p_2/p_1$$

since the density of the gas is proportional to the pressures p_1 and p_2 in the middle sections of the first and second columns.

For small values of a and C, the pressure in the columns decreases from p_{in} to p_{out} by an almost linear law. Under these conditions, taking the total length of the two columns of the circulation scheme as equal to unity, it is possible to write approximately:

$$p_1 = p_{in} - (p_{in} - p_{out})/4 = (3C/4 + 1/4)\, p_{out}$$
$$p_2 = p_{in} - 3(p_{in} - p_{out})/4 = (C/4 + 3/4)\, p_{out}$$

This gives

$$a_{opt} = 2(C - 1)/(3C + 1) \qquad (10)$$

Thus increase in the pressures at the inlet and outlet of the circulation scheme for a given pressure drop makes it possible to achieve values of C close to unity, leading to a corresponding decrease in the factor b_0. Complete elimination of the effect of pulse broadening of the chromatographic zone is achieved, however, by the pulse contraction of the zone, taking place when part of the gas stream is removed after the first column of the circulation scheme.

These ideas were verified[91] using a circulation scheme with controlled gas removal. The dependence of n on m, recorded under these conditions, was linear (straight line in Fig.4) over a fairly wide range of values of m (up to 19 half-cycles).

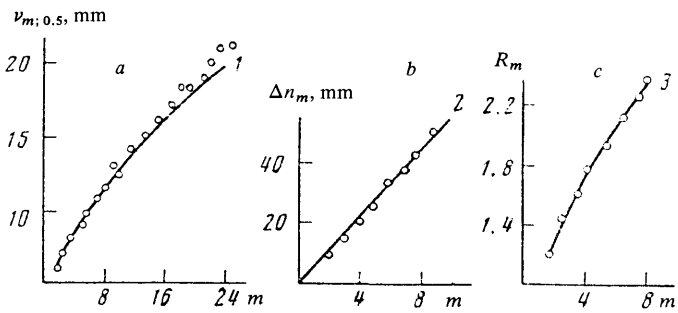


Figure 5. Dependence of the peak width at half-height $\nu_{m;0.5}$ (a), the distance between the maxima of the peaks Δn_m (b), and the degree of separation R_m (c) on the number of half-cycles m: *1*, *2*, *3*) theoretical curves corresponding to Eqns.(1), (2), and (3); the experimental points are marked with circles. Conditions: the column parameters are the same as those in Fig.2; $p_{in} = 0.82$ MPa, $C = 1.29$, $b_0 = 1.01$ for $a_{opt} = 12\%$.

Fig.5 gives the dependence of ν_m, Δn_m, and R_m on m, obtained for $b_0 = 1.01$ and $a_{opt} = 12\%$. The experimental points were found to be close to the theoretical curves *1* and *3* for ν_m and R_m, constructed using Eqns.(1) and (3), and to the theoretical curve *2* for Δn_m, constructed from Eqn.(2).

†The term "non-pulse chromatography" is possibly not entirely appropriate, since when the carrier gas moves from one column to another, its velocity undergoes an abrupt change at the moment when the tap is turned, that is the pulses are preserved. The term "non-pulse chromatography" reflects the fact that the pulse effects, which altered the principal regular features characteristic of the chromatographic process with circulation, disappear.

A decrease in the value of a_{opt} is extremely important in preparative chromatography. According to Eqn.(10), for $C = 1.06$ the value of a_{opt} would be reduced to 3%. On preparative columns[97] with dimensions 3 × 10 mm containing 20% Apiezon L at $p_{in} = 0.63$ MPa and $C = 1.068$ ($a_{opt} = 2.81 \pm 0.15\%$), a linear relationship was obtained between the number of theoretical plates n (with respect to hexane) and the number of columns m through which the chromatographic zone passed. Under these conditions, the preparative circulation apparatus can be regarded as a system of m columns with identical parameters, connected in series.

The losses ϕ of substance during circulation with removal of part of the gas stream between the columns are given by:[90]

$$\varphi, \% = [1 - (1 - a_{opt}/100)^{m-1}] \cdot 100 \qquad (11)$$

These losses can be eliminated almost completely either by the removal and repeated separation of the material removed, or by using hydrogen or a mixture of nitrogen and hydrogen as carrier gas, combined with a palladium separator.[98,99] The contraction of the chromatographic zone brought about by the pneumatic pulses arising when the circulation tap is turned can to some extent replace the use of thermal pulses.[100,101]

Table 1. Comparison of the parameters of the fine separation of benzene and hexadeuteriobenzene at $k' = 2$ in a long packed column (pc), the columns of a circulation assembly (pcc), and a capillary column with a thick layer of sorbent on the walls (c).

Parameter	Nitrogen			Helium		
	pc	pcc	c	pc	pcc	c
Diffusion coefficient in the gas phase at atmospheric pressure $10D_{g,0}$, $cm^2 s^{-1}$	1.06	1.06	1.06	4.14	4.14	4.14
Viscosity of the gas $10^{10}\eta$, kg s cm^{-2}	2.19	2.19	2.19	2.40	2.40	2.40
Diameter of carrier particles d_p, cm	0.02	0.02	0.02	0.02	0.02	0.02
Diffusion coefficient in the gas phase $10^2 D_g$, $cm^2 s^{-1}$	1.40	2.60	2.10	2.70	5.13	4.20
Permeability coefficient $10^7 K^0$, cm^2	3.95	14.04	16.20	3.95	14.58	16.20
Height equivalent to a theoretical plate HETP, cm	0.118	0.118	0.118	0.118	0.118	0.118
Column length l, cm	10620	425	10620	10620	425	10620
Mean linear velocity of the carrier gas $\bar{u}$, cm s^{-1}	1.40	2.60	3.55	2.70	5.13	7.08
Number of theoretical plates n	90000	3600	90000	90000	3600	90000
Number of half-cycles m	—	25	—	—	25	—
Separation time t_R, h	6.33	3.41	2.42	3.28	1.72	1.25
Duration of a half-cycle Δt, min	—	8.19	—	—	4.13	—
Inlet pressure p_{in}, MPa	1.12	0.47	0.70	2.34	0.97	1.49
Guiochon factor j_{pc}	0.81	1.00	0.84	0.78	1.00	0.80
HETP/$\bar{u}$, s^{-1}	0.084	0.045	0.032	0.043	0.023	0.016
$t_R/(t_R)_c$	2.62	1.41	1.00	2.62	1.38	1.00

Notes: separation factor of the components of the mixture 1.02, separation temperature 338 K, capillary column diameter 0.025 cm, fraction of the cross-section occupied by the gas in the capillary column $\kappa = 0.4$, attainable degree of separation $R = 1$.

Thus the ideas developed above about the effects of the pulse contraction and broadening of chromatographic zones, confirmed experimentally, can be used to estimate the place and importance of CGC relative to other chromatographic methods with similar efficiencies.

5. Comparison of the Parameters of Fine Separation in the Filled Columns of a Circulation Scheme and in Columns of Equivalent Length

Comparison of the parameters of fine separation (separation factor $\alpha - 1 \ll 1$) in circulation chromatography and in long packed columns[102-106] showed[107-109] that for a given degree of separation, the time taken for the analysis of a binary mixture is smaller by a factor of approximately 2–3 in the first case. This advantage of circulation chromatography increases as α approaches unity. Compared with long packed columns, circulation chromatography requires a pressure at the inlet to the column which is smaller by a factor of 3.5–4, and the length of the column can be reduced by a factor of 25–30.

Table 1[109] compares various parameters of fine separation in long packed columns, columns of a circulation assembly, and a capillary column with a thick layer of sorbent on the walls.[110,111] The rates of separation for the last two systems are similar. This is due to the relatively high permeability of a hypothetical column with separating power and analysis time equivalent to those of the columns of the circulation system. The slight increase in the HETP in the range of high velocities, observed in circulation chromatography, is much less than that in long columns. As a result of these factors, it is possible to achieve extremely high values of the efficiency of separation in capillary circulation chromatography on columns with a length of 7.5 m.[35,36]

Thus the method examined has extremely significant advantages over separation in long columns from the viewpoint of the total efficiency, separation time, magnitude of the pressure required, quantity of sorbent used, and necessary column length.

IV. THE EFFICIENCY OF THE COLUMNS IN PREPARATIVE CIRCULATION GAS CHROMATOGRAPHY AND METHODS FOR INCREASING THEIR PRODUCTIVITY

The expression for the HETP of a preparative column can be written as follows[112]

$$\text{HETP} = A^0 + \frac{2\gamma \cdot D_g}{\bar{u}} + \frac{8}{\pi^2}\left(\frac{k'}{1+k'}\right)^2 \frac{d_p^2}{D_g}\bar{u} + \frac{2k'}{3(1+k)^2}\frac{d_l}{D_l}\bar{u} + \frac{C_0 d^2}{4D_g}\bar{u}$$

where A^0 is the constant in the Van Deemter equation, γ the sinuosity coefficient, d_l the thickness of the liquid film, D_l and D_g the diffusion coefficients in the liquid and gas phases respectively, C_0 a constant, and d the column diameter.

For preparative columns containing 1–5% or less of the liquid phase,[113] by analogy with analytical columns, it is possible to write

$$\text{HETP} = \frac{2\gamma D_g}{\bar{u}} + \left\{\frac{\frac{C_0}{4}\left(\frac{d}{d_p}\right)^2 + \frac{C_0}{2}\left(\frac{d}{d_p}\right)^2 k' + \left[\frac{C_0}{4}\left(\frac{d}{d_p}\right)^2 + 0.81\right](k')^2}{(1+k')^2}\right\}\frac{d_p^2}{D_g}\bar{u} \qquad (12)$$

When the columns are carefully filled, the efficiences of preparative columns with relatively small diameters are comparable to those of analytical columns. If it is assumed that

$$\frac{C_0}{4}\left(\frac{d}{d_p}\right)^2 = 0.9$$

Eqn.(12) gives

$$\text{HETP} = \frac{2\gamma D_g}{\bar{u}} + \frac{0.9 + 1.8k' + 1.71(k')^2}{(1+k')^2} \cdot \frac{d_p^2}{D_g}\bar{u}$$

The form of the equation obtained is similar to that of the equation for analytical columns.[109]

It has been shown[114] that

$$\bar{u}_{pc} = 0.3\frac{\alpha-1}{d_p}[K^0(D_{r,0})_{pc}(p_{out})_{pc}/\eta]^{1/2}\{(k')^2/[0.9+1.8k'+1.71(k')^2]\}^{1/2} \quad (13)$$

where the subscript "pc" refers to the packed column. Substituting Eqn.(13) in the equation[115]

$$\Pi \approx 5\cdot 10^{-2}\left[\frac{d(\alpha-1)}{R}\right]^2 \varkappa c_g \bar{u}\frac{k'}{1+k'}$$

where Π is the productivity of the preparative chromagraphic assembly, and c_g the equilibrium concentration of the first and second components in the gas phase, gives

$$\Pi_{pc} \approx 1{,}5\cdot 10^{-2}\left[\frac{d(\alpha-1)}{R}\right]^2\frac{\alpha-1}{d_p}\varkappa c_g[K^0(D_{g\,0})_{pc}(p_{out})_{pc}/\eta]^{1/2}[\chi(k')]_{pc}$$

where

$$[\chi(k')]_{pc} = \{(k')^3/(1+k')^2[0.9+1.8k'+1{,}71(k')^2]\}^{1/2}$$

For the circulation system (subscript "pcc")

$$\Pi_{pcc} \approx 1{,}5\cdot 10^{-2}\left[\frac{d(\alpha-1)}{R}\right]^2\frac{\alpha-1}{d_p}\varkappa c_g\left[\frac{K^0_{pce}(D_{g\cdot 0})_{pc}(p_{out})_{pc}}{\eta}\right]^{1/2}[\chi(k')]_{pc}$$

where K^0_{pce} is the permeability coefficient of a hypothetical column equivalent to that used in the circulation system.

With allowance for the loss of substance during circulation (Eqn.(11)), the ratio of the productivities of the circulation system and the long packed column is given by

$$\left[\frac{\Pi_{pcc}}{\Pi_{pc}} = \frac{1}{[C_{pcc}]^{(n-1)/2}}\frac{1}{2.12}\left[\frac{C_{pcc}-1}{C_{pcc}+1}\frac{1}{j_{pc}(\alpha-1)}\frac{1+k'}{k'}\right]^{1/2}\right.$$

where j_{pc} is the Guiochon factor.[116]

These arguments show that for a given total efficiency and similar parameters of the columns used for the separation of substances with very similar properties ($\alpha = 1.02$), the productivity of long columns[117-119] is 2–2.5 times that of a circulation system. The productivity per unit volume of the sorbent,[47,120] however, is ~5 times greater for separation using circulation. This last feature is of considerable importance, since a decrease in the volume of sorbent is not only economical but also leads to a decrease in the volume of the apparatus and the expenditure of work and time in the preparation of the columns.

The efficiency and separating power of columns with length 2–4 m and diameter 10 mm in the preparative separation of mixtures with $1.02 < \alpha < 1.07$ by CGC have been studied.[121] Under conditions in which the removal of gas between the columns was negligibly small (~0.1% of the main stream), increase in the pressure at the outlet from the columns leads to an increase in the overall efficiency n and to an increase in the number of possible half-cycles m. At the same time there is an increase in the time taken for circulation, so that the productivity of the system for a constant volume of specimen added $M_0 = \text{const}$ decreases. Increase in M_0 leads to a decrease in the number of half-cycles and the number of theoretical plates.

Under the conditions of non-pulse circulation chromatography, the removal of gas leads to an additional decrease in productivity. In this case, however, there is a marked increase in the overall efficiency of the separation and an increase in the possible number of cycles. For large volumes of the added specimen and $C_{pcc} = 1.1$, the effect of the pulse broadening of the zone is of secondary importance, and a decisive contribution to the decrease in the overall efficiency is made by the influence of the volume of the specimen added.

The results show that it is appropriate to use CGC to separate compounds with very similar properties under non-pulse circulation conditions.

The decrease in the productivity of the circulation assembly compared with long columns can be avoided by the periodic introduction of the original mixture and removal of the separated components in semi-continuous circulation systems. This method has been used[4,122-124] to separate the alkali metals and various isotopes by ion-exchange chromatography.

For gas chromatography, a method for the semi-continuous separation of mixtures has been proposed,[51] in which, as the specimen is transferred from one column to another during circulation, a fresh portion of the mixture being separated is introduced each time into the supply section, situated between the maxima of the peaks of the components being separated. Subsequently, beginning from the moment when the total width of the zone becomes equal to the length of the chromatographic column, the ends of the chromatographic band are cut off, and the pure components are collected. The overall distribution curve of the component streams with periodic additional supply shows a clearly defined maximum, whose position coincides with the supply section (as a consequence of the superposition of a large number of Gaussian curves).

Circulation chromatography in which the enriched ends of the chromatographic band are cut off is characterised by a high purity of the products obtained. For the usual method of removing the separated zones of the chromatographic compounds, this quantity is given by the equation[125]

$$X_p = 1 - \frac{1}{2(2\pi R)^{1/2}}e^{-2R^2} \quad (14)$$

The value $R = 1$ from Eqn.(14) corresponds to the value $X_p \times 100 = 97.3\%$. The same quantity for circulation chromatography in which the enriched ends of the chromatographic band are cut off is given by the expression[97,126]

$$X'_p = e^{8R(R+1)}/(1+e^{8R(R+1)})$$

For $R' = 1$ the value obtained is $X'_p \times 100 = 99.99998\%$.

For $X_p = X'_p = 99.97\%$, the values obtained are $R \cong 2.8$ and $R' \cong 0.65$ using a column approximately ten times shorter in the circulation scheme.[97]

Thus a brief theoretical examination of the application of the circulation method with periodic additional supply, in which the ends of the chromatographic band are cut off, shows not only an increase in productivity but also the possibility of using this form of CGC to obtain substances with a high purity (≥99.97%).

V. SEPARATION OF ISOTOPICALLY SUBSTITUTED COMPOUNDS

In gas chromatography, the separation of isotopically substituted compounds is one of the most complex problems, requiring the use of highly efficient columns. Unfortunately, an increase in the separation factor by the use of selective liquid phases is almost impossible in this case, because of the extremely small magnitude of the isotope effects in the solution process.[127-129] In other words, change in the nature of the absorbent or liquid phase and the associated change in the adsorptive or solvent power cannot ensure success in the separation of compounds containing different isotopes of a given element.[130] Thus in the search for ways of solving this problem, the need to increase the efficiency of the chromatographic columns used is the most important feature to be considered.

In gas–liquid and gas–adsorption capillary chromatography, the efficiency of the columns can be increased by modifying the inner surface of the walls of the capillaries in different ways, or by depositing sorptive layers of different materials on the walls.[130]

Isotopically substituted compounds can be separated without using long capillary and packed columns of small diameter, by using short packed columns included in a circulation assembly. In the early stages of the development of circulation chromatography, fairly long columns were used. This made it possible to decrease the rate of broadening of the chromatographic band throughout the entire length of the column when the circulation tap was turned. The first isotopic separations[82] of methane, n-butane, cyclobutane, and their deuteriated and tritiated analogues were carried out on 15 m columns at atmospheric pressure at the outlet.

Columns with length 8 m, containing a solution of silver nitrate in ethylene glycol as stationary phase, have been used[83,84] for the gas-chromatographic separation of the isotopically substituted ethylenes C_2H_4, C_2H_3D, and $C_2H_2D_2$. The analysis using the circulation technique was more rapid than that using one long column; this is particularly important in the gas chromatography of isotopic molecules containing radioactive isotopes with short half-lives.

An attempt has been made[85] to separate the isotopes of carbon (^{12}C and ^{13}C) and sulphur (^{32}S and ^{34}S) as their volatile fluorides. The separation was carried out with Maxwell's circulation scheme[44] using two 8 m columns containing Porapak. Appreciable enrichment of the isolated fractions in the individual isotopes was achieved. Compounds labelled with radioactive isotopes (^{14}C, ^{35}S) were later analysed[131] on an automatic circulation gas radiochromatograph.

Table 2. Principal characteristics of the preparative gas-chromatographic separation of various isotopically substituted organic compounds by CGC on columns with dimensions 4 m × 23 mm.

Mixture being separated	Stationary phase	v, ml	w, %	L, m	α	$10^{-3}n$	HETP, mm	R
CH_3COCH_3—CD_3COCD_3	LAC-3R-728	0.90	39.9	108	1.012	35.5	3.0	0.56
C_6H_{12}—C_6D_{12}	LAC-3R-728	0.85	50.4	84	1.014	44.5	1.9	0.74
$C_6H_5CH_3$—$C_6D_5CD_3$	DC-550	0.50	44.0	84	1.013	44.0	1.9	0.68
C_6H_6—C_6D_6	DC-550	0.55	40.3	92	1.011	48.0	1.9	0.60
$C_6H_5C_2H_5$—$C_6D_5C_2H_5$	DC-550	0.50	28.7	128	1.006	74.5	1.7	0.41

Symbols: v is the volume of the specimen added, w the yield of separated products, and L the total column length traversed by the zones.

The separation of the carbon isotopes ^{12}C and ^{13}C as the oxide on molecular sieves, and the separation of the neon isotopes ^{20}Ne and ^{22}Ne, have been carried out;[132] appreciable enrichment in the isotopes was again achieved. Two columns with lengths of 0.5 m containing molecular sieves have been used[77] to separate the o- and p-isomers of H_2 and D_2. The separation factors were 1.032 for o- and p-hydrogen, 1.024 for protium deuteride and deuterium, and 1.019 for o- and p-deuterium.

The effects of pulse broadening and contraction of the chromatographic zones and the related increase in the efficiency of the process made it possible to separate benzene and hexadeuteriobenzene, and also benzene and trideuteriobenzene,[133] on columns with dimensions 4 m × 4 mm containing squalane as liquid stationary phase. In the last case, the compounds being separated passed through a total column length equivalent to 100 m, and the efficiency of the separation was ~120 thousand t.p. This high efficiency of separation was made possible by using non-pulse circulation chromatography conditions, characterised by a linear relationship between the number of theoretical plates and the number of columns passed through. The analytical separation of a number of oxygen-containing isotopically substituted organic compounds has been carried out:[69,134] C_2H_5OH–C_2D_5OD, CH_3COCH_3–CD_3COCD_3, iso-C_3H_7OH–iso-C_3D_7OD, under non-pulse CGC conditions.

The possibilities provided by preparative CGC for separating isotopically substituted organic compounds have been studied by the present authors.[135–137] The principal characteristics of the preparative gas-chromatographic separation of the mixtures studied by CGC are given in Table 2,[138] which shows that the efficiency of preparative separation by CGC reached several tens of thousands of t.p., which is 10–20 times the efficiency of long packed columns (dimensions 20 m × 9 mm),[113] and is comparable with the possibilities provided by capillary chromatography. Mass-spectrometric analysis showed that the purity of the fractions obtained was not lower than 95–97%. Fig.6 gives fragments of the chromatogram obtained in the preparative separation of toluene and perdeuteriotoluene.

As already noted, the productivity of circulation gas-chromatographic systems used to separate compounds with similar properties, requiring a highly efficient process, depends to a large extent on the quantity of eluate removed to maintain non-pulse chromatographic conditions. For the preparative separations listed in Table 2, this quantity was 2.0–2.4% of the total carrier-gas volume for a ratio of the

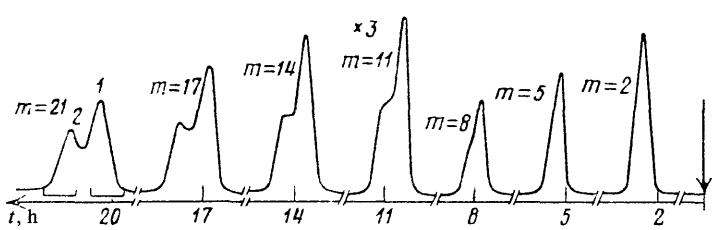


Figure 6. Fragments of the chromatogram for the preparative CGC separation of a mixture of octadeuteriotoluene (*1*) and toluene (*2*) on 4 m × 23 mm columns filled with DC-550 (15%). Conditions: temperature of the columns 105 °C, p_{in} = 0.64 MPa, C = 1.04, carrier-gas (nitrogen) velocity 400 ml min^{-1}, fraction of gas removed ~2%, initial loading 0.5 ml, yield of separated products 44%.

inlet and outlet pressures $C = 1.04-1.05$ and a pressure at the column inlet not exceeding 0.64 MPa. A decrease in the quantity C as a result of an increase in the inlet and outlet pressures (for the same given pressure drop) makes it possible to decrease the quantity of gas removed between the columns and hence to increase the productivity of the circulation assembly. Thus an increase in the pressure at the inlet into the system to, for example, 1.33 MPa (keeping the rate of supply of carrier gas at the outlet from the system unchanged) decreases the value of C to 1.023. This in turn makes it possible to decrease the quantity of gas removed between the columns and to decrease the loss during the separation of the above mixtures by 13–17%.

VI. SEPARATION OF ORGANIC COMPOUNDS WITH SIMILAR STRUCTURES AND PROPERTIES

A field in which circulation chromatography is irreplaceable is the fine preparative separation of the isomers of volatile organic compounds. In a number of cases, the similarity in the properties of these isomers is even closer than that for isotopic molecules. The difficulties of separating isomers are also increased by the fact that newly synthesised organic compounds are often available only in very small quantities, corresponding to fractions of a gram or milligrams.

The problem of determing the isomeric composition of newly synthesised organic compounds is now being solved using highly efficient capillary chromatography, but the problem of the preparative separation of isomers with similar properties still remains one of the most difficult unsolved problems in organic chemistry. At the same time, the high efficiency of separation characteristic of CGC makes it possible to solve the problem of both the analytical and the preparative separation of isomeric structures for the resolution of a wide range of problems encountered in present-day organic chemistry.

Thus the composition of the products of the intramolecular acylation of ω-(5-methylthienyl-2)-alkanoic acids with side chains of different length has been studied[139] by the chromatographic analysis of the isomeric macrocyclic ketones with a thiophene ring. The isomeric cyclic thienones were separated on 3 m × 4 mm columns with a sorbent containing 3% SE-30 at a temperature of 235 °C, a carrier-gas velocity of 55 ml min^{-1}, $p_{in} = 0.89$ MPa, and $C = 1.25$. Twelve half-cycles in 2 h gave the value $R = 1.04$ for $\alpha = 1.023$. The efficiency of separation amounted to ~64 thousand t.p. Good results have been obtained in the separation of the geometric isomers of high-boiling saturated aliphatic acids on columns containing 5% Apiezon L.[94] Methyl oleate and methyl elaidate were separated at 220 °C after 11 half-cycles at $p_{in} = 0.70$ MPa and $p_{out} = 0.62$ MPa. The isomeric methyl linoleates were separated under similar conditions. The overall efficiency of separation in these experiments reached ~83 thousand t.p.

The *cis*- and *trans*-isomers of 1-ethyl-4-isopropylcyclohexane, 2-t-butyltetrahydrofuran, and 3-t-butylcyclopentanol have been separated on columns with length 3.5 m and diameter 10 mm, filled with the carrier Chezasorb with 5% XE-60.[70] An efficiency of separation of 3–8 thousand t.p. was achieved using a 20 mg specimen after 8–9 half-cycles. The same authors carried out the analytical separation of a mixture of the methyl esters of 1,3-dimethylcyclohex-3-ene-1-carboxylic and 1,4-dimethylcyclohex-3-ene-1-carboxylic acids — the isomeric products of a diene synthesis — with $\alpha = 1.044$. An efficiency of ~23.5 thousand t.p. with a separation factor of 1.04 was achieved after 8 half-cycles in 1.5 h.

A mixture of propylene oxide and propionaldehyde has been separated[140] by circulation gas chromatography on a column with Chromosorb W containing 30% dinonyl phthalate. The same author separated *m*- and *p*-xylenes after 3 half-cycles on two 45 cm columns filled with a sorbent containing 7.5% bentone-34 and 14.25% MS-555 silicone oil. The micropreparative separation of the isomeric tetramethylbenzenes

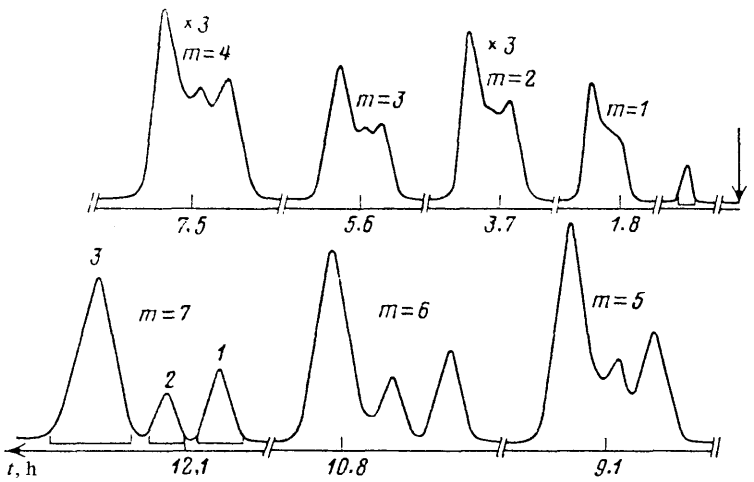


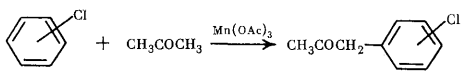
Figure 7. Fragments of the chromatogram of the preparative CGC separation of a mixture of *p*- (*1*), *m*- (*2*), and *o*-chlorobenzyl methyl ketones (*3*) on 4 m × 20 mm columns filled with LAC-3R-728 polyester (12%). Conditions: temperature of the columns 220 °C, $p_{in} = 0.58$ MPa, $p_{out} = 0.54$ MPa, carrier-gas (nitrogen) velocity 380 ml min^{-1}, removal of gas between columns 3.0%, original loading 0.5 ml, yield of separated products 83%.

durene and isodurene with an efficiency of separation of 26 thousand t.p. has been described.[115]

One of the advantages of CGC is its universal nature. As a result of the high efficiencies achieved by repeating the separation cycle, it is possible to obtain good results without using highly selective stationary liquid phases. Thus mixtures of the isomeric aromatic hydrocarbons: *m*- and *p*-xylenes, *p*-xylene and ethylbenzene,[137] and isomeric tetramethylbenzenes[115] were separated equally successfully by preparative methods on stationary phases which are not highly selective (LAC-3R-728, DC-550, and PEG-6000 respectively).

Circulation chromatography has also been used to study the kinetics of chemical reactions in reaction gas chromatography. Thus in a study of the kinetics of the Diels–Alder reaction between isoprene and maleic anhydride, the latter was deposited on Chromosorb P as stationary phase in the form of a solution in tricresyl phosphate. The change in the concentration of the volatile component isoprene was followed from the change in the area of the peaks recorded during circulation.[141]

To study the products of homolytic substitution in chlorobenzene by acetonyl radicals generated in the acetone–$Mn(OAc)_3$–AcOH redox system at 70 °C according to the published scheme,[142] the present authors[138] carried out the preparative separation of the mixtures of isomers formed, using highly efficient CGC.



The separation was carried out in an all-glass assembly with a gas-stream separating tap placed outside the thermostat.[75] Fragments of the chromatogram obtained are shown in Fig.7. Practically complete separation of all three isomers with an efficiency of separation of 12.5 thousand t.p. for the *p*-isomer was achieved after seven half-cycles, which corresponds to a total path length of the zones through the column of 28 m. The separation factors of the isomers according to the analytical chromatograms were 1.046 for *m*- and *p*-chlorobenzyl methyl ketones and 1.051 for the *o*- and *m*-structures.

A series of preparative separations of stereoisomeric derivatives of 1,3-dioxolane was described by the present authors.[143] These five-membered cyclic acetals are of interest as model systems for the study of the stereochemistry of various natural physiologically active substances. Calculations of the thermodynamic parameters of solution[143] showed that the diastereoisomers of 2,4,5-tri-isopropyl-, 2-phenyl-4,5-di-isopropyl-, and 2-phenyl-2-methyl-4,5-di-isopropyl-1,3-dioxolanes, synthesised by the acid-catalysed condensation of *meso*- and *dl*-2,5-dimethylhexan-3,4-diols with the corresponding carbonyl compounds, have extremely similar properties. The similar di- and trialkyl(aryl)-derivatives of 1,3-dioxolane also have similar properties,[144–147] and this made it necessary to use preparative columns with lengths of 20 m and 7.5 m. Examples of the preparative CGC separation of 2-substituted 4,5-di-isopropyl-1,3-dioxolanes are shown in Fig.8. The separation was carried out on a circulation assembly with the valve switching system described in Ref.137. The separation factor for the *syn*- and *anti*-isomers of 2-phenyl-4,5-di-isopropyl-1,3-dioxolane, according to the analytical chromatogram, was 1.048. The efficiency of the preparative separation at the seventh half-cycle reached 14.5 thousand t.p. (with respect to the *syn*-isomer). The separation of the *syn*- and *anti*-isomers of 2,4,5-tri-isopropyl-1,3-dioxolane, for which the differences in the free energies of solution in the temperature range 110–140 °C do not exceed 38–55 J $mole^{-1}$ (that is $\alpha = 1.011$–1.019), required an efficiency of more than 50 thousand t.p.

In the experiments described above, the quantity of products being separated simultaneously was 0.5–1.0 g, which corresponds to the scale of the laboratory studies usually carried out in synthetic organic chemistry at the present time. CGC may also find extensive application, however, in special preparative studies involving the accumulation of large quantities of individual isomers for a more detailed study of their physicochemical properties, for use in subsequent synthetic studies, or for carrying out biological tests.

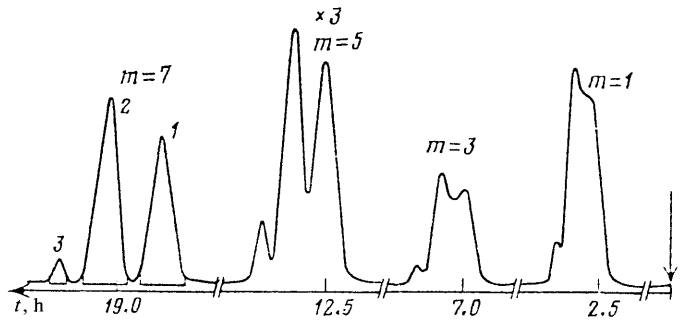


Figure 8. Fragments of the chromatogram of the preparative CGC separation of a mixture of *cis-anti*- (*1*), *cis-syn* (*2*), and *trans*-2-phenyl-4,5-di-isopropyl-1,3-dioxolanes (*3*) on 4 m × 23 mm columns filled with DC-550 polyphenylsiloxane oil (15%). Conditions: temperature of the columns 210 °C, $p_{in} = 0.64$ MPa, $p_{out} = 0.59$ MPa, carrier-gas (nitrogen) velocity 480 ml min^{-1}, removal of gas between columns 3.3%, original loading 0.6 ml, yield of separated products 79.5%.

The present authors used a semi-continuous version of highly efficient CGC to separate a mixture of the *cis*- and *trans*-isomers of 2,5-dimethyl-1,3-octathiane.[138] The preparative assembly operated at an inlet pressure of 0.59 MPa and an outlet pressure of 0.56 MPa, the quantity of carrier gas removed was 2%, the temperature of the columns 140 °C, the carrier-gas (nitrogen) velocity 300 ml min^{-1}, and the magnitude of the original specimen 0.65 ml. The stationary phase was Carbowax-20M (10%) in columns with dimensions 4 m × 23 mm. Beginning from the eighth half-cycle, when the band of chromatographic compounds had spread throughout the entire length of the column, the circulation was continued under non-pulse chromatographic conditions. The introduction of fresh portions of the mixture being separated and the removal of the enriched ends of the chromatographic band were carried out in each half-cycle in quantities of 50 μl. By the seventeenth half-cycle, ten additional quantities of the mixture had been introduced, and ~0.5 ml of separated products had been collected, corresponding to 43% of the total loading. Analysis of the collected fractions by capillary chromatography (column length 40 m, efficiency 70 thousand t.p. with respect to benzene) showed that the compounds were practically pure, containing not less than 99.6% of the individual components.

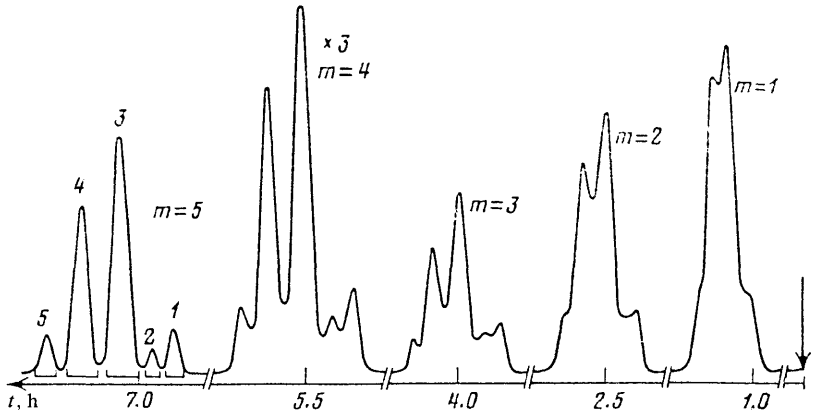


Figure 9. Fragments of the chromatogram of the preparative CGC separation of the high-boiling fraction of the distillate of the light oil, purified from phenol, of the tar from the semi-coking of Cheremkhovo coal on 4 m × 23 mm columns filled with DC-550 polyphenylsiloxane oil (15%). Conditions: temperature of columns 235 °C, p_{in} = 0.64 MPa, p_{out} = 0.58 MPa, carrier-gas (nitrogen) velocity 450 ml min^{-1}, removal of gas between columns 3.7%, original loading 0.5 ml; *1*) benzothiophene, *2*) methylbenzothiophene, *3*) β-methylnaphthalene, *4*) α-methylnaphthalene, *5*) biphenyl; efficiency of separation after the fifth half-cycle 12.5 thousand t.p. (with respect to β-methylnaphthalene); yield of separated products 84%.

Highly efficient preparative CGC has also been used to study the composition of various products of the treatment of coal. The importance of the complete and rational utilisation of the products of the processing of coal is making it necessary to develop accessible methods for separating and analysing the compounds originating from coal. The present authors and the Technological Laboratory of the Institute of Organic Chemistry of the Academy of Sciences of the USSR have studied the composition of the light oil, purified from phenol, with boiling point up to 250 °C, obtained as a fraction of the tar from the medium-temperature coking of coal from the Cheremkhovo deposit (Irkutsk coalfield).[138] The results obtained in the course of this study showed the promising possibilities provided by the use of preparative CGC at the stage involving the separation of the substances being studied from the semi-coking products. CGC showed that the light oil from the tar obtained in the medium-temperature coking of Cheremkhovo coal contains normal saturated, cyclic, and aromatic hydrocarbons, heterocyclic sulphur-containing compounds of the thiophene and benzothiophene series, and also condensed aromatic hydrocarbons, mainly of the naphthalene series. Fig.9 gives a chromatogram for the preparative separation of one of the narrow fractions of light oil from the tar obtained in the thermal degradation of Cheremkhovo coal.

Until recently, the separation of enantiomers of α-aminoacids by gas–liquid chromatography on optically active stationary phases was carried out using highly efficient capillary columns. Thanks to the availability of highly selective chiral liquid phases,[148] the number of which has increased considerably in recent years,[149–153] it has been possible to use for this purpose not only capillary columns but also fairly efficient short packed columns.[154–157] In this connection, promising possibilities are provided by the preparative separation of racemates using short packed columns with a selective chiral stationary phase included in a circulation scheme.

CGC has been used[158] to separate the enantiomers of alanine (Fig.10), valine, norvaline, leucine, norleucine, alloisoleucine, and isoleucine as the isopropyl esters of the N-trifluoroacetyl derivatives of N-stearyl-L-valine t-butylamide as liquid phase. The experiments were carried out as models for the subsequent preparative separation of the optically active compounds from the racemic mixtures, and it was shown[158] that the proposed chiral separating agent successfully combines a fairly high thermal stability (≧170 °C) with a high separating power. Even when the chiral diamide was mixed with achiral polyethylene glycol in the ratio 1 : 1, it was possible to achieve the practically complete separation of the enantiomers of a number of aminoacids.

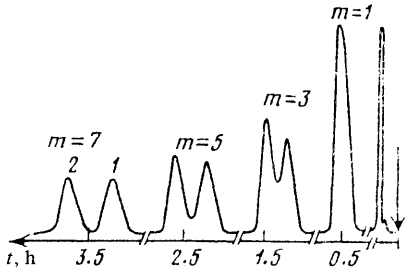


Figure 10. Fragments of the chromatogram of the CGC separation of the racemic isopropyl ester of N-trifluoroacetylalanine. Conditions: 2 m × 3 mm columns, N-stearyl-L-valine t-butylamide (4.6%) and PEG-20 M (4.4%) on N-Super Chromaton, temperature of columns 137 °C, p_{in} = 0.69 MPa, p_{out} = 0.65 MPa, carrier-gas (helium) velocity 35 ml min^{-1}, removal of gas between columns 2.5%, specimen volume 1 μl, *1* and *2*) *D*- and *L*-isomers respectively.

Subsequently, columns with dimensions 2.5 m × 8 mm with a sorbent containing 10% of the pure chiral stationary phase were used for the preparative separation of the racemates of a number of α-aminoacids.[159] Fig.11 gives fragments of t

chromatogram of the preparative separation of the racemate of norvaline by CGC. The optical purity of the separated enantiomers was followed from the dispersion of the optical rotation of the fractions collected and the pure *L*- or *D*-forms of the standard in solutions with similar concentrations, and it was shown that there was good agreement between the dispersion curves of the standard specimens and the corresponding separated fractions of the racemates, and also between the enantiomer pairs themselves. For a loading of the original racemate of 90–120 mg, the yield of the fractions separated, with allowance for the losses associated with the removal of part of the gas stream to achieve non-pulse chromatography conditions, is 70–90%. The productivity of the circulation assembly used, based on a standard LKhM-8MD gas chromatograph, corresponded to 0.4–0.6 g of racemate per day. A number of methods are available for increasing the productivity of the preparative separation of enantiomers, for example by the use of semi-continuous circulating systems. The above data make it possible to regard the preparative CGC of optically active substances as a new method for separating racemic mixtures, which has not been used before in organic chemistry and which may find a place in practical studies in fine organic synthesis and biochemistry.

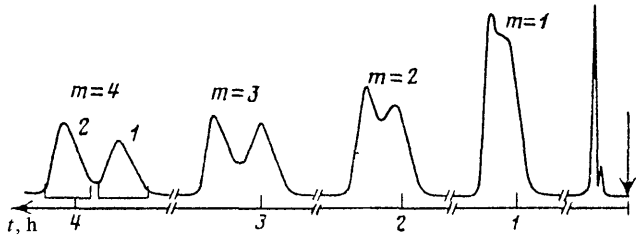


Figure 11. Fragments of the chromatogram of the preparative CGC separation of the racemic isopropyl ester of N-trifluoroacetylnorvaline on 2.5 m × 8 mm columns filled with N-stearyl-L-valine t-butylamide (10%) on Chromaton N-AW DMCS. Conditions: temperature of the columns 170 °C, p_{in} = 0.66 MPa, p_{out} = 0.60 MPa, carrier-gas (nitrogen) velocity 70 ml min^{-1}, removal of gas between columns 3.7%, original loading 90 mg; *1* and *2*) *D*(-) and *L*(+) isomers respectively; yield of separated products 90%.

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The ideas developed in the last ten years on the effects of the pulse contraction and broadening of chromatographic zones, the optimum conditions of non-pulse circulation chromatography established on this basis, and the new apparatus and procedures for carrying out circulation chromatography have laid the foundations for the use of this method for the highly efficient preparative separation of compounds with extremely similar properties.

Preparative circulation chromatography under non-pulse conditions, characterised by a linear increase in the number of theoretical plates with increase in the number of cycles, makes it possible to achieve an efficiency of separation comparable with that of capillary chromatography, using specimens which are larger by factors of 10^6–10^7. This makes it possible, within an acceptable time, to obtain the pure separated components in quantities sufficient for subsequent physical, chemical, and biological studies.

The extension of theoretical knowledge and the improvement of circulation techniques and procedures are opening up extensive possibilities for the further development of the circulation method in various forms of chromatography — gas, vapour-phase, liquid — as a method for the physicochemical study, analysis, accumulation, and preparative separation of compounds with similar structures and properties.

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Zelinskii Institute of Organic Chemistry
Academy of Sciences of the USSR,
Moscow

Analytical Chemistry Department,
Sechenov Medical Institute 1,
Moscow

Russian Chemical Reviews

October 1984

Translated from *Uspekhi Khimii*, 53, 1601-1624 (1984)

U.D.C. 541.12.036+541.49

The Temperature Jump Method and Its Application in the Study of Complex Formation

V.I.Pogonin and A.K.Chibisov

The present state of the apparatus used in the temperature jump method (methods for rapid heating, recording concentration changes, and collecting and processing experimental data) has been described. The formal kinetics of chemical relaxation on complex formation (relaxation times and amplitudes) have been examined. The mechanisms of complex formation by metal ions with various ligands, based on data obtained by the temperature jump method, have been discussed.
The bibliography contains 118 references.

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I. INTRODUCTION

In the last twenty years, considerable progress has been made in the study of fast reactions, due primarily to the development of methods for studying them.[1,2] With the development of pulse, relaxation, flow, electrochemical, radiofrequency spectroscopic, and other methods,[2] it has now become possible to study intermediate short-lived products (excited molecules and complexes, ions, radicals, etc.), and also to study the kinetics and mechanism of reactions taking place in times of down to 10^{-14} s.

Among chemical relaxation methods, which are widely and successfully used to study the kinetics of reversible reactions in which equilibrium is established rapidly, an important place is occupied by the temperature jump method. The relative simplicity of the method makes it widely accessible for the study of redox and protolytic reactions, complex formation, enzyme reactions, hydrolysis, etc.

The present review examines the temperature jump method and its application in the study of complex formation in solution. The latest experimental techniques are described, and the formal kinetics of chemical relaxation on complex formation are examined. There is practically no information on these topics in the Soviet literature.

As an illustration of the application of the temperature jump method in the study of fast reactions, the process of complex formation by metal ions with various ligands is examined (the last review in this field was published in 1968 [3]).

II. THE TEMPERATURE JUMP METHOD

The temperature jump method is based on the temperature dependence of the equilibrium constant of a reaction. In accordance with the Van't Hoff isobar equation, the change in the equilibrium constant produced by change in temperature

is revealed by a corresponding change in the equilibrium concentrations of the reagents and reaction products. If the temperature of a system in equilibrium is increased rapidly (temperature jump), a relaxation process involving the establishment of new equilibrium concentrations begins to take place in the system. The rate of this process and the magnitude of the change in concentration are determined by the properties of the system being studied. Various methods for rapidly increasing the temperature, and methods for recording the concentration changes and for processing the experimental data, are examined below.

1. Methods for Rapidly Increasing the Temperature

The internal energy of a system is determined by the sum of the translational, rotational, vibrational, and electronic energies. Each of the components of the internal energy can be expressed in terms of the distribution of the populations of the corresponding levels and determines the corresponding temperature of the system: translational, rotational, vibrational, and electronic, which are equal to one another at thermodynamic equilibrium. An increase in one of these temperatures is brought about by a selective change in the distribution of the populations of the corresponding energy levels, but as a result of rapid internal relaxation and exchange of energy between the molecules in the liquid phase, temperature equilibrium is re-established in a time of <1 ns.[4]

Thus the temperature of a system can be increased rapidly and effectively by introducing energy in any of the above forms into the system. Thus different methods are available for rapidly increasing the temperature: a) Joule heating and a heat-exchange temperature jump (excitation as a result of a change in the rate of translational movement of the molecules); b) microwave heating (rotational excitation); c) laser temperature jump (vibrational excitation); and d) pulse ultraviolet irradiation (electronic excitation).

Joule heating is the simplest and most widely encountered method for obtaining a temperature jump. The heating is brought about by the discharge of a high-voltage condenser through the electrolyte solution. The discharge is usually controlled by a discharger or thyratron. The use of Joule heating makes it possible to obtain a temperature jump of 3–10 K in 1–10 μs in a system with a volume of 0.1–25 ml.[2] Decreasing the heating time is a technically difficult problem. A temperature jump apparatus has been described,[5] which can heat 0.2 ml of solution through 3 K in 300 ns by using a low-induction condenser, gas-filled dischargers of the "krytron" type, and a specially designed cell. A coaxial line, matched with the cell, is also used as condenser, to obtain a temperature jump of 10 K in 50 ns.[6] Decrease in the length of the coaxial line, and suppression of stray effects of electro-luminescence and electrodichroism, produced in solutions at electric field intensities greater than 60 kV cm^{-1}, made it possible to decrease the heating time to 10 ns.[7]

The heat-exchange temperature jump method uses two water-baths, kept at different constant temperatures.[8] The temperature jump can be made fairly large, and both heating and cooling of the system being studied are possible. The heat-exchange temperature jump method makes it possible to study relaxation processes with times of 0.5 s or more.

The temperature jump method is usually employed to study systems in equilibrium at normal atmospheric pressure. Temperature jump apparatus with Joule heating, in which the cell design makes it possible to study chemical relaxations at a pressure of up to 3×10^8 Pa, have also been described.[9–11]

Microwave heating, or heating as a result of the dielectric relaxation of a liquid, is achieved by using a pulse superhigh-frequency (SHF) generator. For water, as for most polar solvents, the maximum absorption of microwave energy takes place at ~10 GHz. Apparatus with SHF heating[12–15] usually employs magnetrons, operating under pulse conditions with an output energy of up to 0.5 J; the solution is heated through 0.2–2 K in 0.25–5 μs.

Rapid heating of a solution can be achieved by the absorption of the light pulse of, for example, a neodymium or ruby laser (laser temperature jump), for which the wavelength of the radiation is 1.06 μm or 0.694 μm respectively. For most solvents, however, the absorption at these wavelengths is extremely small, so that it is impossible to obtain a significant temperature jump. Thus when a neodymium laser operating under free lasing conditions[16,17] or under modulated Q conditions,[18,19] was used, the temperature jump for aqueous solutions was ≤ 0.6 K. A temperature jump of more than 1 K using a neodymium laser with modulated Q is prevented both by the plasma produced when the powerful laser radiation is focussed and by the two-photon processes excited in the system being studied.[20]

One method for increasing the efficiency of laser heating is by introducing into the system substances (absorbers) which strongly absorb the laser radiation. These substances should be chemically inert with respect to the solvent and the system being studied, should be transparent in the range of the spectrum where the changes in absorption are being recorded, and should effectively transform the absorbed light energy into heat during the laser pulse.[16] The absorbers proposed for use with a ruby laser include copper nitrate and Naphthol Green B for aqueous solutions,[16,21] and also vanadyl phthalocyanine for aprotic solvents.[22] The temperature jump achieved by this method was 2–5 K. The heating time was determined by the duration of the laser pulse and amounted to 300–500 μs. The heating time cannot be decreased using a laser with modulated Q, because of the bleaching of the absorber at high laser energy densities.

A temperature jump of 3–10 K has been obtained using lasers with modulated Q by employing Raman neodymium lasers. The radiation of the neodymium laser, operating under modulated Q conditions, is transformed into radiation of longer wavelength by passing through an appropriate Raman medium. A laser temperature jump apparatus using liquid nitrogen ($\lambda_{rad} = 1.41$ μm) as Raman medium has been described.[23–29] In this case, 0.1 ml of aqueous solution was heated through 5–9 K in 30 ns. A laser temperature jump apparatus using gaseous hydrogen ($\lambda_{rad} = 1.89$ μm) at a pressure of 8×10^6 Pa as Raman medium has been described.[30–32] The temperature jump was 2–3 K in 18–50 ns. The use of hydrogen does not require cryogenic techniques, as in the case of liquid nitrogen. 24 different media for Raman lasers, and also a laser temperature jump apparatus using liquid nitrogen, with subnanosecond resolution (heating time 180 ps), have been described.[33] The possible use of excimer lasers to achieve a temperature jump has been examined.[24] An iodine laser ($\lambda_{rad} = 1.315$ μm)[34–36] and a neodymium laser operating at 1.32–1.36 μm without additional transformation[37] have also been described.

The use of laser heating also makes it possible to study relaxation processes at pressures of up to $(2–3) \times 10^8$ Pa.[16,17]

Pulse ultraviolet lamps, whose radiation is readily absorbed by solvent molecules, can also be used to heat solutions rapidly. A spiral pulse ultraviolet lamp, through which a condenser with a capacity of 10 μF, charged to a voltage of 15 kV, is discharged, has been described.[38] In temperature

jump apparatus with ultraviolet irradiation, an aqueous solution has been heated through 1 K in 5 μs.

The characteristics of different methods for obtaining a temperature jump are compared in Table 1.

2. Methods for Recording Changes in Concentration

The most convenient and widely used method for recording the changes in the concentrations of the reagents or reaction products is the spectrophotometric method. In this method, a light beam (usually monochromatic) is passed through the cell containing the solution being heated, and falls on a photoreceiver (for example a photomultiplier instrument), whose output is transferred to an oscillograph, which records the change with time in the transmission in the cell. Methods for supplying the photomultiplier instrument, and the amplifiers and integrating and differentiating filters used in fast-action absorption spectrophotometry, have been described in detail.[2,39]

When an equilibrium between reagents and reaction products is displaced, their concentrations change by an amount Δc_i, leading to a change in the optical density of the system D in accordance with the Lambert–Beer law:

$$\Delta D = \sum_i \varepsilon_i \Delta c_i l$$

where ε_i is the molar absorptivity of the absorbing species, and l the optical path length of the cell. If $\Delta D \ll D$, the relative change in the light intensity is given by

$$\frac{\Delta I}{I_0} = -2.304 \frac{\Delta D}{D} \cdot D \cdot 10^{-D}$$

Differentiating this expression with respect to D and assuming that the ratio $\Delta D/D$ is constant gives the value of the optical density $D = 0.434$ corresponding to the maximum change in intensity ΔI. The maximum signal/noise (S/N) ratio for a system in which particles of only one kind absorb is observed at $D = 0.868$.[40] These conclusions apply to systems whose composition is fixed. For systems with varying composition, usually studied by the temperature jump method, the calculation of the optimum values of the S/N ratio is extremely complicated. The calculation has been carried out using a computer for the single-stage protolytic reaction of Methyl Orange (pH indicator).[41] The calculation showed that the conditions under which the highest values of the intensity of the photometric signal and the S/N ratio are reached depend on the absorption by the particles $\varepsilon_i l$, the pH of the solution, and the analytical concentration of the reagent. The optimum value of the optical density is approximately half that given in Ref. 40.

The sensitivity limit of a temperature jump apparatus with spectrophotometric recording is usually 10^{-3}–10^{-4} optical density units, and is determined by the S/N ratio. This ratio in turn depends on the transmission band Δf of the recording scheme, the quantum efficiency of the photo-receiver, and the intensity of the probing light source. The transmission band is usually controlled during the experiment by integrating and differentiating filters, and is kept in the following range:

$$(3-10)\,\tau_f^{-1} > \Delta f > (0.1-0.3)\,\tau_s^{-1}$$

where τ_f and τ_s are the relaxation times of the fastest and slowest of the processes being studied. The photo-receiver is usually a photomultiplier, for which the quantum yield of the photo-cathode is 1–30%. A silicon photo-diode, combined with a low-noise amplifier, has been used.[42] This apparatus makes it possible to record changes in absorption in the range 1 μs–5 ms with a better S/N ratio than a photomultiplier.

The S/N ratio can be increased by increasing the brightness of the probing light source. Increasing the brightness of a halogen lamp by a factor of ~5 with an increase in the supply voltage from 12 V (nominal conditions) to 16 V (forced conditions) in a time of 300 ms has been proposed.[43] Xenon arc lamps are usually supplied from stabilised current sources; by applying rectangular pulses of increased current with a duration reaching 1 ms, it is possible to obtain an increase in the brightness of the lamp by a factor of 50–700 in the blue and ultraviolet ranges of the spectrum.[44–46] This method makes it possible to improve the S/N ratio by a factor of $(I_f/I_{st})^{1/2}$, where I_f and I_{st} are the intensities of the emission from the lamp under forced and stationary conditions respectively. With pulse supply of the probing lamp, it is necessary to use special active schemes to compensate automatically the constant component of the output current of the photomultiplier[47] or a high-frequency passive filters.[48]

Table 1. Comparison of methods for obtaining a temperature jump.

Heating method	τ_h, s	ΔT, K	V_{min}, ml	Solvent requirements	Possibility of using conductometric recording	Possibility of operating under frequency conditions with accumulation and averaging	Possibility of application to heterogeneous systems	Technical simplicity of heating apparatus	Notes
Joule	10^{-8}–10^{-5}	5–10	0.1–10	polar, ionic strength 0.05–0.5 M	no	no	no	simple, particularly for the range 10^{-6}–1 s	side reactions with electrolysis products and the salts added to create the required ionic strength are possible
SHF	10^{-6}	0.2–2	0.07–0.2	polar, any ionic strength	yes	yes	yes	complex	—
Laser	10^{-8}–10^{-11}	2–9	0.01–0.1	none	yes	yes	yes	complex, particularly when liquid N_2 is used as the Raman medium	requires a laser with wavelength in the range of infrared absorption by the solvent; cavitation is possible; heating is non-uniform
Ultraviolet	$5 \cdot 10^{-6}$	5	5	none	yes	—	—	simple	simultaneous photochemical reactions are possible

Notes: τ_h = heating time; V_{min} = minimum solution volume.

In temperature jump apparatus with spectrophotometric recording, the reaction cell is usually illuminated by a monochromatic light beam, and this makes it possible to record the relaxation process at only one wavelength in one experiment. A series of experiments is necessary to record the spectrum of relaxation amplitudes. An apparatus using a polychromator has been described,[49] which makes it possible to record the kinetic curves at several wave-lengths simultaneously. The output from the polychromator passes to 10–30 photo-electronic multipliers, connected to digital memory blocks, in which the information is recorded simultaneously in the course of one experiment. A similar apparatus using a dissector instead of a set of photomultipliers has been described.[50] Spectrophotometric recording has a high selectivity, and this is of considerable importance in the study of multi-equilibrium systems.

Conductometric recording is used in addition to spectrophotometric recording in the temperature jump method. In conductometric recording, two planar inert electrodes (usually of platinum or gold), to which a probing voltage is applied, are placed in the reaction cell. Slow relaxation processes are observed using a constant current,[51] and fast processes using rectangular current pulses,[52] which makes it possible to decrease the polarisation effects at the electrodes. Best results are obtained, however, using a varying probing voltage; in this case, a high-frequency Wheatstone bridge is used to increase the sensitivity. The bridge is supplied from the generator of a variable (usually sinusoidal) voltage with a frequency of from 100 kHz to 10 MHz, and a narrow-band amplifier and oscillograph are connected to its diagonals. On temperature perturbation of the reaction system, the bridge is unbalanced; the change in the amplitude of the high-frequency voltage reflects the relaxation process.

Conductometric recording is used with microwave heating,[12–14] optical heating using lasers,[16,18] and pulse ultraviolet lamps.[38] Conductometric recording has a higher sensitivity (reaching 0.001%) than spectrophotometric recording, and, other conditions being equal, it makes it possible to obtain a better S/N ratio.[52]

Recording changes in fluorescence can be an extremely effective method for observing chemical relaxation in the temperature jump method. A temperature jump method with Joule heating, using recording of the changes in concentration both from the absorption and from the intensity of the fluorescence, has been described.[53] The cell had four optical windows, two of which were used for the spectrophotometric recording, and the other two were used to record both the polarised and the non-polarised fluorescence emission. An apparatus of this kind can also be used to record changes in the light scattering.

3. The Collection and Processing of the Experimental Data

In the general case, the kinetic curve obtained in temperature jump experiments represents the sum of several exponents:

$$S(t) = \sum_i A_i \, e^{-t/\tau_i}$$

where A_i and τ_i are the initial amplitude and time of the relaxation of the ith equilibrium. The traditional method for processing the kinetic curves involves photographing the curve on the oscillograph screen and then transforming it to a semilogarithmic scale. If the relaxation process is characterised by a single relaxation time, the transformed line is strictly linear. If there is a set of relaxation times, the transformed line is a curve. In this case, graphical separation of the terms included in the sum $S(t)$ is possible with the condition that the values of τ_i differ by factors of not less than 2–3.

The question of the accuracy of the graphical separation of two or more exponential curves has been discussed.[54,55]

Since the graphical procedure described above is extremely laborious, other methods have been proposed for determining relaxation times. Thus a method has been proposed[56] for processing a kinetic curve characterised by a single relaxation time. The photographic image of the curve is projected on to the screen of an oscillograph, and an exponentially damping voltage, produced by means of an RC-circuit, is supplied to the oscillograph input. The values of R and C are varied to achieve superposition of the curves and hence find the relaxation time $\tau = RC$. A scheme has been proposed,[57] in which the voltage from the output of the temperature jump apparatus is applied to the input Y of the oscillograph, and the voltage from the generator of the exponentially quenching voltage is applied to the input X. When the parameters are equal, a Lissajou figure in the form of a straight line is observed on the oscillograph screen. The uncertainty of the determination of the relaxation time by the two methods is 10%.

A widely encountered method for collecting and processing the experimental data involves the use of a computer. The signal being studied is transformed into digital form by means of an analogue–digital transformer and recorded in the memory of the computer, which processes the kinetic curve using special programs. A method involving the use of a digital oscillograph connected to a mini-computer has been described.[58] With a large number of breakdown points (up to 4000), the subsequent mathematical treatment to a large extent makes it possible to avoid periodic and random noise in the signal, to improve considerably the signal/noise ratio, and to determine the parameters of the relaxation process with a high accuracy.

Digital recording readily makes it possible to accumulate and average the signals from a large number (N) of repeat experiments, leading to an increase in the S/N ratio by a factor of $(N)^{1/2}$. This method, combined with preliminary analogue integration of the signal,[59] makes it possible to increase the accuracy of the processing of the experimental data. Accumulation and averaging of the signal are particularly easily carried out in apparatus with microwave[12,14,15] and laser[37] heating, since the excitation sources used in these methods operate under frequency conditions. Using accumulation of the data, it has been possible to achieve a sensitivity of 0.01% in the microsecond time range and of 0.1% in the nanosecond range.

The digital information is usually processed by the least-squares method for non-linear curves, and various methods for doing this on a computer have been described.[60–62]

III. THE KINETICS OF CHEMICAL RELAXATION ON COMPLEX FORMATION

In the general case, complex formation between metal ions $M^{m+}(aq)$ and a ligand $L^{n-}(aq)$ is a multi-stage reversible reaction:

$$M^{m+}(aq) + L^{n-}(aq) \rightleftharpoons ML^{(m-n)+} \qquad (1)$$

If the equilibrium constants of the reactions (1) depend on temperature, heating displaces the equilibrium. If the system is in equilibrium at an initial temperature T_1, then a rapid change (jump) in temperature by δT leads to the production of non-equilibrium conditions. The time taken to reach the new equilibrium state corresponding to the final temperature

T_2 (the relaxation time τ) in general depends on the rate constants of the stages of reaction (1) and on the equilibrium concentrations of the reagents. The change in the equilibrium concentrations of the reagents (the relaxation amplitude), reached at the moment when the new equilibrium state is established, depends on the magnitude and sign of the enthalpy changes of the separate stages of the reaction, and also on the equilibrium constants and the equilibrium concentrations of the reagents. Expressions for the relaxation times and relaxation amplitudes in complex formation reactions with different degrees of complexity are given below.[63,64]

1. Relaxation Time and Relaxation Amplitudes in a Single-Stage Reaction

In the simplest case, complex formation can be represented as a single-stage reversible reaction:

$$M^{m+}(aq) + L^{n-}(aq) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} ML^{(m-n)+} \qquad (2)$$

The expression for the relaxation time is obtained from the equation describing the kinetics of the reaction after the temperature jump (or after any other short-lived perturbation of the system, leading to displacement of its equilibrium).[63] The expression for the rate of reaction (2)†

$$-d[M]/dt = k_{12}[M][L] - k_{21}[ML]$$

written in terms of the equilibrium (at the final temperature) concentrations $[\bar{M}]$, $[\bar{L}]$, and $[\overline{ML}]$ and in terms of the small changes in the concentrations $\delta[M]$, $\delta[L]$, and $\delta[ML]$, due to the displacement of the equilibrium, has the form:

$$-\frac{d[\bar{M}]}{dt} - \frac{d\,\delta[M]}{dt} = k_{12}[\bar{M}][\bar{L}] - k_{21}[\overline{ML}] + k_{12}\delta[M][\bar{L}] + k_{12}\delta[L][\bar{M}] + k_{12}\delta[M]\delta[L] - k_{21}\delta[ML] \qquad (3)$$

For small deviations from the equilibrium position, it is possible to neglect the term $k_{12}\delta[M]\delta[L]$ in Eqn.(3). The material balance equation

$$\delta[M] + \delta[ML] = 0;\ \delta[L] + \delta[ML] = 0 \qquad (4)$$

gives

$$-\frac{d\,\delta[M]}{dt} = k_{12}([\bar{M}] + [\bar{L}])\,\delta[M] + k_{21}\delta[M] \qquad (5)$$

Thus the expression for the relaxation time has the form

$$\tau = \{k_{12}([\bar{M}] + [\bar{L}]) + k_{21}\}^{-1} \qquad (6)$$

The values of the rate constants k_{12} and k_{21} of the forward and back reactions are found from the graphical plot of τ^{-1} against $[\bar{M}] + [\bar{L}]$. Since the values of $[\bar{M}] + [\bar{L}]$ are usually unknown, k_{12} and k_{21} are determined by the widely used technique in which one of the reagents, for example L, is taken in excess. In this case

$$\tau^{-1} = k_{12}[L]_0 + k_{21} \qquad (7)$$

where $[L]_0$ is the initial concentration of the ligand, and $[L]_0 \gg [M]_0$.

To find k_{12} and k_{21}, it is also convenient to use the expression

$$\tau^{-2} = k_{12}^2([M]_0 - [L]_0)^2 + 2k_{12}k_{21}([M]_0 + [L]_0) + k_{21}^2 \qquad (8)$$

obtained from Eqn.(6). In this case, the values $k_{12}k_{21}$ are found from the graphical plot of τ^{-2} against $[M]_0 + [L]_0$ for a fixed value of the difference $[M]_0 - [L]_0$. In the particular case where $[M]_0 = [L]_0$, expression (8) is simplified to

$$\tau^{-2} = 4k_{12}k_{21}[M]_0 + k_{21}^2 \qquad (9)$$

and when $[L]_0 \gg [M]_0$ it becomes Eqn.(7).

Eqn.(6) leads to an important conclusion about the conditions for achieving the extremal value of τ (τ resonance). Expressing the equilibrium concentrations $[M]$ and $[\bar{L}]$ in terms of the initial concentrations $[M]_0$ and $[L]_0$ and the equilibrium constant $K = k_{12}/k_{21}$ and using Eqn.(6) gives

$$\tau k_{12} = \{([M]_0 - [L]_0 + K^{-1})^2 + 4K^{-1}[L]_0\}^{-1/2} \qquad (10)$$

From Eqn.(10) it follows that τk_{12} has a maximum value for $[M]_0 = [L]_0$ (Fig.1):

$$\tau_{max} k_{12} = (K^{-2} + K^{-1}[L]_0)^{-1/2} \qquad (11)$$

Eqn.(11) can also be obtained from Eqn.(9), which is simplified when $K^{-1} \ll [M]_0$, $[L]_0$ (for a strongly bonded complex)

$$\tau_{max} k_{12} = \frac{1}{2}\left(\frac{K}{[L]_0}\right)^{1/2}$$

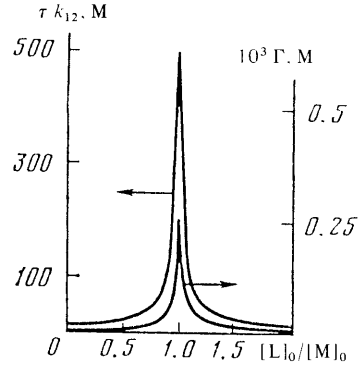


Figure 1. Resonance of τ and Γ for a strongly bonded complex, $K = 10^5$ litre mole^{-1}; $[M]_0 = 0.1$ M.[63]

The relationship between the relaxation amplitude and the parameters of reaction (2) can be established as follows. From the expression for the equilibrium constant

$$K = [\overline{ML}]/[\bar{M}][\bar{L}] \qquad (12)$$

it follows that

$$\frac{\delta K}{K} = \frac{\delta[ML]}{[\overline{ML}]} - \frac{\delta[M]}{[\bar{M}]} - \frac{\delta[L]}{[\bar{L}]} \qquad (13)$$

The material balance equation (4) and Eqn.(13) gives:

$$\frac{\delta K}{K} = \delta[ML]\left(\frac{1}{[\bar{M}]} + \frac{1}{[\bar{L}]} + \frac{1}{[\overline{ML}]}\right)$$

On the other hand, the Van't Hoff isobar equation

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H}{RT^2}$$

gives:

$$\frac{\delta K}{K} = \frac{\Delta H}{RT^2}\delta T$$

Thus the relaxation amplitude is given by the expression

† For simplicity, the indices $m+$, $n-$ and $(m-n)+$ for M, L, and ML are omitted.

$$\delta[ML] = \Gamma \frac{\Delta H}{RT^2} \delta T \qquad (14)$$

where $\Gamma = (1/[\bar{M}] + 1/[\bar{L}] + 1/[\overline{ML}])^{-1}$ is the transfer function of reaction (2).

Thus the change in the concentration of the complex (or the reagents) is directly proportional to the product of the enthalpy of the reaction, the change in temperature as a result of heating, and the value of the transfer function. The values of the relaxation amplitudes are important for finding the change in the enthalpy of the reaction. It follows from Eqn.(14) that the enthalpy of the reaction can be determined from direct measurements of $\delta[ML]$ (or $\delta[M]$, $\delta[L]$, the quantity δT, and the value of Γ.

A knowledge of the value of Γ is of considerable importance for finding the optimum conditions for measuring the relaxation amplitude. Using Eqn.(12), it is possible to write the expression for Γ as:

$$\Gamma = \frac{K[\bar{M}][\bar{L}]}{1 + K([\bar{M}] + [\bar{L}])} \qquad (15)$$

In the particular case where $[\bar{M}] = [\bar{L}]$, Eqn.(15) becomes

$$\Gamma = \frac{K[\bar{M}]^2}{1 + 2K[\bar{M}]} \qquad (16)$$

Introducing the parameter $\alpha = [\bar{M}]/[M]_0$ gives from Eqn.(16)

$$\Gamma = \frac{\alpha(1-\alpha)}{2-\alpha}[M]_0$$

from which the maximum value of $\Gamma/[M]_0 = 0.173$ for $\alpha = 0.586$.

The transfer function Γ can be expressed in terms of the initial concentrations $[M]_0$ and $[L]_0$. For this purpose, the expression for Γ is written in the form:

$$\Gamma = \frac{[\overline{ML}]K^{-1}}{[\bar{M}] + [\bar{L}] + K^{-1}}$$

obtained from Eqns.(12) and (15). Expressing $[\overline{ML}]$ in terms of $[M]_0$, $[L]_0$ and K gives:

$$\Gamma = \frac{1}{2K} \cdot \frac{[M]_0 + [L]_0 + K^{-1}}{\{([M]_0 - [L]_0)^2 + 2K^{-1}([M]_0 + [L]_0) + K^{-2}\}^{1/2}} - 1 \qquad (17)$$

Particular cases give the following results:

1) for $[M]_0 \gg [L]_0$

$$\Gamma = \frac{1}{2K}[([M]_0 + K^{-1})^{1/2} - 1] \qquad (18)$$

2) for $[M]_0 = [L]_0 \neq K^{-1}$

$$\Gamma = \frac{1}{2K}\left[\frac{2[M]_0 + K^{-1}}{(4K^{-1}[M]_0 + K^{-2})^{1/2}} - 1\right] \qquad (19)$$

3) for $[M]_0 = [L]_0 = K^{-1}$

$$\Gamma = 0.6K^{-1} \qquad (20)$$

Eqns.(18)–(20) can be used to calculate Γ, which is necessary to find ΔH for the reaction.

It is of interest to examine the case where a strongly bonded complex is formed, $[M]_0 + [L]_0 \gg K^{-1}$; in this case, from Eqn. (17):

$$\Gamma = \frac{1}{2K}\left(\frac{[M]_0 + [L]_0}{[([M]_0 - [L]_0)^2 + 2K^{-1}([M]_0 + [L]_0)]^{1/2}} - 1\right)$$

If the initial concentrations are equal, $[M]_0 = [L]_0$ (resonance of Γ), it follows that:

$$\Gamma \simeq {}^1/_2([M]_0/K)^{1/2}$$

It is obvious that the value of Γ for $[M]_0 = [L]_0$ is much greater than the limiting values of Γ for $[M]_0 \gg [L]_0$ or $[L]_0 \gg [M]_0$, that is for a given value of $[M]_0$ the plot of Γ against $[L]_0/[M]_0$ passes through a maximum, which is reached at $[L]_0/[M]_0 = 1$ (see Fig.1).

2. Relaxation Times and Relaxation Amplitudes in Two-Stage Reactions

A two-stage reaction (for example the formation of a unidentate complex) is described by the equation:

$$\underset{(I)}{M^{m+}(aq) + L^{n-}(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{(II)}{M^{m+}(aq)L^{n-}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{(III)}{ML^{(m-n)+}} \qquad (21)$$

where $M^{m+}(aq)L^{n-}$ and $ML^{(m-n)+}$ are the outer-sphere and inner-sphere complexes. Stage (I) → (II) involves the loss of a water molecule from the hydration layer of the ligand, whereas stage (II) → (III) involves the loss of a water molecule from the hydration layer of the metal cation.

An approach to the derivation of an expression for the relaxation times in the case where the rates of reactions (I) ⇌ (II) and (II) ⇌ (III) are close to one another[63] is examined below. For small departures from the equilibrium position, the rate of reaction (21) is described by the system of equations #:

$$\begin{cases} -\dfrac{d\delta[M]}{dt} = k_{12}\delta[M]([\bar{M}] + [\bar{L}]) - k_{21}\delta[M(aq)L] \\ \dfrac{d\delta[ML]}{dt} = k_{23}\delta[M(aq)L] - k_{32}\delta[ML] \end{cases}$$

which with allowance for the material balance equation

$$\delta[M] + \delta[M(aq)L] + \delta[ML] = 0 \qquad (22)$$

becomes

$$\begin{cases} \dfrac{d\delta[M]}{dt} + \{k_{12}([\bar{M}] + [\bar{L}]) + k_{21}\}\delta[M] + k_{21}\delta[ML] = 0 \\ \dfrac{d\delta[ML]}{dt} + k_{23}\delta[M] + (k_{23} + k_{32})\delta[ML] = 0 \end{cases} \qquad (23)$$

The solution of this system of differential equations has the form:

$$\begin{cases} \delta[M] = \delta[M]^0 e^{-t/\tau} \\ \delta[ML] = \delta[ML]^0 e^{-t/\tau} \end{cases} \qquad (24)$$

Substituting Eqns.(24) in Eqns.(23) gives the relaxation times τ_1 and τ_2, $\tau_1 < \tau_2$, in the form:

$$\tau_1^{-1} = \frac{1}{2}\{\Sigma k + [(\Sigma k)^2 - 4\pi k]^{1/2}\} \qquad (25)$$

$$\tau_2^{-1} = \frac{1}{2}\{\Sigma k - [(\Sigma k)^2 - 4\pi k]^{1/2}\} \qquad (26)$$

where

$$\Sigma k = \tau_1^{-1} + \tau_2^{-1} = k_{12}([\bar{M}] + [\bar{L}]) + k_{21} + k_{23} + k_{32}$$
$$\Pi k = \tau_1^{-1}\tau_2^{-1} = k_{12}(k_{23} + k_{32})([\bar{M}] + [\bar{L}]) + k_{21}k_{32}$$

The values of the rate constants of reaction (21) are found graphically from the linear dependence of the sum $\tau_1^{-1} + \tau_2^{-1}$ on $([\bar{M}] + [\bar{L}])$ and the linear dependence of the product $\tau_1^{-1}\tau_2^{-1}$ on $([\bar{M}] + [\bar{L}])$.

It is important to examine the expressions for τ_1^{-1} and τ_2^{-1} for the following particular cases:

1) $k_{12}([\bar{M}] + [\bar{L}] + k_{21} \gg k_{23}, k_{32}$,
that is reaction (I) ⇌ (II) is more rapid than reaction (II) ⇌ (III) In this case the expression for the relaxation times have the form

$$\tau_1^{-1} = k_{12}([\bar{M}] + [\bar{L}]) + k_{21}$$
$$\tau_2^{-1} = k_{23}\frac{K_1([\bar{M}] + [\bar{L}])}{1 + K_1([\bar{M}] + [\bar{L}])} + k_{32}$$

where $K_1 = k_{12}/k_{21}$;

2) $k_{21} + k_{23} \gg k_{12}([\bar{M}] + [\bar{L}])$, k_{32},
that is the state of the complex M(aq)L can be regarded as

For simplicity, the indices $m+$, $n-$, and $(m-n)+$ for M, L, and ML are omitted.

stationary. In this case,

$$\tau_1^{-1} = k_{21} + k_{23}$$
$$\tau_2^{-1} = \frac{k_{12}k_{23}([\bar{M}] + [\bar{L}])}{k_{21} + k_{23}} + \frac{k_{21}k_{32}}{k_{21} + k_{23}} \quad (27)$$

Eqn.(27) can also be obtained by the method of stationary concentrations. It is simplified in the limiting cases where $k_{21} << k_{23}$ and $k_{21} >> k_{23}$. For $k_{21} << k_{23}$, that is when the formation of the inner-sphere complex ML is more rapid than the dissociation of the outer-sphere complex M(aq)L to the solvated ions,

$$\tau_2^{-1} = k_{12}([\bar{M}] + [\bar{L}]) + \frac{k_{21}k_{32}}{k_{23}}$$

In the opposite situation, when $k_{21} >> k_{23}$, Eqn.(27) becomes

$$\tau_2^{-1} = k_{23}K_1([\bar{M}] + [\bar{L}]) + k_{32}$$

3) $k_{23} + k_{32} >> k_{12}([\bar{M}] + [\bar{L}])$, k_{21}, that is reaction (II) ⇌ (III) is more rapid than reaction (I) ⇌ (II). In this case,

$$\tau_1^{-1} = k_{23} + k_{32}$$
$$\tau_2^{-1} = k_{12}([\bar{M}] + [\bar{L}]) + k_{21}k_{32}/(k_{23} + k_{32})$$

Table 2 gives expressions for the relaxation times in two-stage reactions taking place by different mechanisms. Thus the reaction

$$\begin{cases} LH^+ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} L + H^+ \\ L + M \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML \end{cases} \quad (A)$$

corresponds to the typical case of complex formation involving a ligand L present in equilibrium with the protonated form LH^+. In the reaction

$$\begin{cases} L' \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} L \\ L + M \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML \end{cases} \quad (B)$$

the ligand is the reactive tautomer L, present in equilibrium with the tautomer L′ which does not form complexes. In the reaction

$$\begin{cases} M + L_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} ML_1 \\ ML_1 + L_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML_1L_2 \end{cases} \quad (C)$$

successive addition of the two ligands L_1 and L_2 takes place.

It is convenient to examine the expressions for the relaxation amplitudes for the example of the two-stage reaction (21) with the condition that there is an excess concentration of one of the reagents, for example the ligand ($[L]_0 >> [M]_0$).[63] In this case, from the expressions for the equilibrium constants, defined as

$$K_1 = \frac{k_{21}}{k_{12}[L]_0} = \frac{[\bar{M}]}{[\overline{M(aq)L}]}; \quad K_2 = \frac{k_{23}}{k_{32}} = \frac{[\overline{ML}]}{[\overline{M(aq)L}]}$$

it follows that the maximum changes in the concentrations $\delta[M]^0$ and $\delta[ML]^0$ can be written as

$$\delta[M]^0 = K_1\delta[M(aq)L]^0 + \delta K_1[\overline{M(aq)L}] \quad (28)$$

$$\delta[ML]^0 = K_2\delta[M(aq)L]^0 + \delta K_2[\overline{M(aq)L}] \quad (29)$$

The material balance equation (22) and Eqns.(28) and (29) give the following expressions for the relaxation amplitudes

$$\delta[M]^0 = [\bar{M}]\frac{(1 + K_2)\cdot\delta K_1/K_1 - K_2\cdot\delta K_2/K_2}{1 + K_1 + K_2} \quad (30)$$

$$\delta[ML]^0 = [\overline{ML}]\frac{(1 + K_1)\cdot\delta K_2/K_2 - K_1\cdot\delta K_1/K_1}{1 + K_1 + K_2} \quad (31)$$

$$\delta[M(aq)L]^0 = -[\overline{M(aq)L}]\frac{K_1\cdot\delta K_1/K_1 + K_2\cdot\delta K_2/K_2}{1 + K_1 + K_2} \quad (32)$$

Since the relative changes in the equilibrium constants K_1 and K_2 are proportional to the enthalpies of the reactions

$$\delta K_1/K_1 = (\Delta H_1/RT^2)\delta T,\ \delta K_2/K_2 = (\Delta H_2/RT^2)\delta T$$

where ΔH_1 and ΔH_2 are the enthalpies of reactions (II) ⇌ (I) and (II) ⇌ (III), it follows that the expressions for the relaxation amplitudes (30)–(32) represent essentially the dependence of these amplitudes on the enthalpies ΔH_1 and ΔH_2.

Table 2. Expressions for the relaxation times for the two-stage reactions (A)–(C) for different relationships between the rate constants of the separate stages; $K_1 = k_{12}/k_{21}$, $K_2 = k_{32}/k_{23}$.

Reaction	Conditions	τ_1^{-1}	τ_2^{-1}
(A)	$k_{12} + k_{21}([\bar{L}] + [\bar{H}^+]) \gg k_{23}([\bar{L}] + [\bar{M}]),\ k_{32}$	$k_{12} + k_{21}([\bar{L}] + [\bar{H}^+])$	$k_{23}\left([\bar{L}] + [\bar{M}]\frac{K_1 + [\bar{L}]}{K_1 + [\bar{L}] + [\bar{H}^+]}\right) + k_{32}$
	$k_{23}([\bar{L}] + [\bar{M}]) + k_{32} \gg k_{12},\ k_{21}([\bar{L}] + [\bar{H}^+])$	$k_{23}([\bar{L}] + [\bar{M}]) + k_{32}$	$k_{12} + k_{21}\times\left([\bar{L}] + [\bar{H}^+]\frac{K_2 + [\bar{L}]}{K_2 + [\bar{L}] + [\bar{M}]}\right)$
(B)	$k_{12} + k_{21} \gg k_{23}([\bar{L}] + [\bar{M}]),\ k_{32}$	$k_{12} + k_{21}$	$k_{23}\left([\bar{L}] + \frac{K_1[\bar{M}]}{1 + K_1}\right) + k_{32}$
	$k_{23}([\bar{L}] + [\bar{M}]) + k_{32} \gg k_{12},\ k_{21}$	$k_{23}([\bar{L}] + [\bar{M}]) + k_{32}$	$k_{12} + k_{21}\frac{K_2 + [\bar{L}]}{K_2 + [\bar{L}] + [\bar{M}]}$
(C)	$k_{12}([\bar{M}] + [\bar{L}_1]) + k_{21} \gg k_{23}([\overline{ML_1}] + [\bar{L}_2]),\ k_{32}$	$k_{12}([\bar{M}] + [\bar{L}_1]) + k_{21}$	$k_{23}\left([\overline{ML_1}] + [\bar{L}_2]\times\frac{K_1[\bar{M}] + K_1[\bar{L}_1]}{1 + K_1([\bar{M}] + [\bar{L}])}\right) + k_{32}$
	$k_2([\overline{ML_1}] + [\bar{L}_2]) + k_{32} \gg k_{12}([\bar{M}] + [\bar{L}_1]),\ k_{21}$	$k_{23}([\overline{ML_1}] + [\bar{L}_2]) + k_{32}$	$k_{12}([\bar{M}] + [\bar{L}_1]) + k_{21}\frac{K_2 + [\overline{ML_1}]}{K_2 + [\overline{ML_1}] + [\bar{L}_2]}$

In particular, if complex formation is conjugated with the protonation of the ligand, then for a definite value of the ratio $\Delta H_1/\Delta H_2$, a change in the sign of the relaxation amplitudes (a bicipital phenomenon[65–67]) with change in the pH of the medium is possible.

Thus the following reaction can be considered:

$$\begin{matrix} M + L \overset{\Delta H_1}{\rightleftharpoons} ML \\ L + H^+ \overset{\Delta H_2}{\rightleftharpoons} LH^+ \end{matrix} \quad (33)$$

Assuming that the stage involving the protonation of the ligand L is more rapid than the stage involving the formation of the complex ML, and also that complex formation takes place in an excess concentration of the metal, $[M]_0 >> [L]_0$, it follows that the relaxation amplitudes $\delta[H^+]^0$, $\delta[L]^0$, and $\delta[ML]^0$ can be expressed as follows in terms of the transfer function Γ of reaction (33), where $\Gamma^{-1} = [\bar{L}]^{-1} + [\bar{H}^+]^{-1} +$

$[\overline{LH^+}]^{-1}$, and the enthalpies ΔH_1 and ΔH_2:

$$-\delta[H^+]^0 = \Gamma \frac{\Delta H_2}{RT^2}\delta T$$
$$\frac{\delta[ML]^0}{[\overline{ML}]} - \frac{\delta[L]^0}{[\overline{L}]} = \frac{\Delta H_1}{RT^2}\delta T$$

The material balance equation

$$\delta[L]+\delta[ML]+\delta[LH^+]=0$$

gives

$$\delta[ML]^0 = \frac{[\overline{L}][\overline{ML}]}{[\overline{L}]+[\overline{ML}]}\left(\Delta H_1 - \frac{\Delta H_2}{1+\beta}\right)\frac{\delta T}{RT^2} \quad (34)$$

where

$$\beta = \frac{1}{K[\overline{H^+}]} + \frac{[\overline{L}]}{[\overline{H^+}]}, \quad K = [\overline{LH^+}]/[\overline{L}][\overline{H^+}] \quad (35)$$

It follows from Eqns.(34) and (35) that if $\Delta H_2/\Delta H_1 > 1$, then the relaxation amplitude $\delta[ML]^0$ changes sign when

$$[\overline{H^+}] = \frac{K^{-1}+[\overline{L}]}{\Delta H_2/\Delta H_1 - 1}$$

Eqns.(30)–(32) represent the total changes in the concentrations of M, ML, and M(aq)L in reaction (21). Expressions are given below for the relaxation amplitudes in the stages (I) ⇌ (II) (provisionally taken as fast, subscript A) and (II) ⇌ (III) (provisionally taken as slow, subscript B) of reaction (21):

$$\delta[M]^0_A = [\overline{M}]\frac{1}{1+K_1}\cdot\frac{\delta K_1}{K_1}$$
$$\delta[M(aq)L]^0_A = -[\overline{M(aq)L}]\frac{K_1}{1+K_1}\frac{\delta K_1}{K_1}$$
$$\delta[M]^0_B = [\overline{M}]\frac{K_2(K_1\cdot\delta K_1/K_1 - \delta K_2/K_2 - K_1\cdot\delta K_2/K_2)}{(1+K_1)(1+K_1+K_2)} \quad (36)$$

$$\delta[M(aq)L]^0_B = [\overline{M(aq)L}]\frac{K_2(K_1\cdot\delta K_1/K_1 - \delta K_2/K_2 - K_1\cdot\delta K_2/K_2)}{(1+K_1)(1+K_1+K_2)} \quad (37)$$

The amplitude $\delta[ML]^0_B = \delta[ML]^0$ is given by Eqn.(31).

It follows from Eqns.(31), (36), and (37) that to observe stage (II) ⇌ (III) by the temperature jump method it is not necessary that the enthalpy of this stage have a finite value ($\Delta H_2 \sim \delta K_2/K_2 \neq 0$). It follows from Eqn.(31) that for $\Delta H_2 = 0$,

$$\delta[ML]^0 = -[\overline{ML}]\frac{K_1\cdot\delta K_1/K_1}{1+K_1+K_2}$$

that is the relaxation amplitude $\delta[ML]^0$ is determined essentially by the enthalpy ΔH_1 of the stage (I) ⇌ (II). This feature is of considerable practical importance; small relaxation amplitudes can be increased considerably by selecting a stage (I) ⇌ (II) with a high rate of establishment of equilibrium and a high enthalpy value.

3. Relaxation Times in Multi-Stage Reactions

In the general case, the kinetics of multi-stage reactions involving $n+1$ states can be described by a system of n linear differential equations[63]

$$\frac{d[x_i]}{dt} + \sum_{j=1}^{n} a_{ij}[x_j] = 0, \text{ where } i, j = 1, 2, \ldots, n \quad (38)$$

Here, $[x_j] = \delta[c_j] = [c_j] - [\bar{c}_j]$ is the change in the concentration of the jth state for a small displacement of the equilibrium, and a_{ij} is a parameter which depends on the rate constants and the equilibrium concentrations of the states of the multi-stage reaction.

The solution of the system of equations (38) is a set of n exponents of the form:

$$[x_i] = \sum_{j=1}^{n}[x_i]^0_j e^{-t/\tau_j}, \text{ where } i, j = 1, 2, \ldots, n \quad (39)$$

The relaxation times (relaxation spectrum) are found by solving the system of algebraic equations obtained by substituting Eqn.(39) in Eqn.(38).

The most general example of a reaction involving more than two stages is the three-stage reaction of complex formation with a bidentate ligand:

$$M^{m+}(aq) + L^{n-}(aq) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} M^{m+}(aq)L^{n-} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML^{(m-n)+} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} M{=}L^{(m-n)+} \quad (40)$$
(IV) (V) (VI) (VII)

which compared with reaction (21) includes the additional stage (VI) ⇌ (VII) involving the formation of the bidentate complex $M{=}L^{(m-n)+}$, associated with the loss of a second water molecule from the hydration layer of the metal cation. In accordance with the scheme for the solution of Eqns.(38) and (39), the three values of the relaxation times characterising the three-stage reaction (40) are the roots of the cubic equation

$$(1/\tau)^3 + A_1(1/\tau)^2 - A_2(1/\tau) + A_3 = 0$$

where

$$A_1 = k_{12}([\overline{M}]+[\overline{L}]) + k_{21} + k_{23} + k_{32} + k_{34} + k_{43}$$
$$A_2 = (k_{21}+k_{12}([\overline{M}]+[\overline{L}]))(k_{23}+k_{32}) + (k_{23}+k_{32})(k_{34}+k_{43}) + (k_{21}+k_{12}([\overline{M}]+[\overline{L}]))(k_{34}+k_{43}) - k_{21}k_{23} - k_{32}k_{34}$$
$$A_3 = (k_{21}+k_{12}([\overline{M}]+[\overline{L}]))(k_{23}+k_{32})(k_{34}+k_{43}) - (k_{21}+k_{12}([\overline{M}]+[\overline{L}]))k_{32}k_{34} - (k_{34}+k_{43})k_{21}k_{23}$$

The corresponding concentration dependence of the relaxation times τ_1, τ_2, and τ_3, obtained experimentally, and the relationships

$$A_1 = \tau_1^{-1} + \tau_2^{-1} + \tau_3^{-1}$$
$$A_2 = \tau_1^{-1}\tau_2^{-1} + \tau_1^{-1}\tau_3^{-1} + \tau_2^{-1}\tau_3^{-1}$$
$$A_3 = \tau_1^{-1}\tau_2^{-1}\tau_3^{-1}$$

can now be used to determine the values of all six rate constants of reaction (40).

In complex formation, the stages of the reaction often differ considerably in the rates at which equilibrium is established. In this case, the analysis of the relaxation spectrum is much easier. Table 3 gives expressions for three relaxation times, corresponding to fast, medium, and slow stages in the reaction.

A frequently encountered particular case is complex formation (A) (R.p.1612) not accompanied by spectral changes. The kinetics of the establishment of equilibrium can then be followed using an acid–base indicator added to the system. The set of coupled equilibria is represented by the scheme:[2]

$$M + L \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} ML$$
(VIII) (IX)
$$H^+ + L \rightleftharpoons LH^+$$
$$H^+ + Ind \rightleftharpoons Ind\,H^+$$

If the formation of ML is slow compared with the rapid protonation of the ligand L and the indicator Ind, the establishment of equilibrium (VIII) ⇌ (IX) after the temperature jump is followed from the change in the colour of the indicator. The relaxation time is given by the expression

$$\tau^{-1} = k_{12}\left(\frac{[\overline{M}]}{1+\gamma} + [\overline{L}]\right) + k_{21}$$

where

$$\gamma = \frac{[\overline{H^+}]}{K_{LH^+} + \chi[\overline{L}]}; \quad \chi = \frac{K_{IndH^+} + [\overline{H^+}]}{K_{IndH^+} + [\overline{H^+}] + [\overline{Ind}]};$$
$$K_{LH^+} = [\overline{H^+}][\overline{L}]/[\overline{LH^+}]; \quad K_{IndH^+} = [\overline{H^+}][Ind]/[\overline{IndH^+}]$$

If the values of K_{LH^+} and K_{IndH^+} are known, the value of γ can be calculated for any value of the pH of the solution, and this in turn makes it possible to determine graphically the values of k_{12} and k_{21} from the experimentally determined value of τ.

Table 3. Expressions for the relaxation times in the system

$$M(aq) + L(aq) \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} M(aq)L \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} ML \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} M\text{-}L$$

for different ratios of the reaction rate constants*.

Conditions	τ_1^{-1} (fast stage)	τ_2^{-1} (medium stage)	τ_3^{-1} (slow stage)
$k_{12}([\overline{M}]+[\overline{L}])$, $k_{21} \gtrsim k_{23}$, $k_{32} \gtrsim k_{34}$, k_{43}	$k_{12}([\overline{M}]+[\overline{L}])+k_{21}$	$k_{23}\frac{K_1([\overline{M}]+[\overline{L}])}{1+K_1([\overline{M}]+[\overline{L}])}+k_{32}$	$k_{34}\frac{K_1([\overline{M}]+[\overline{L}])K_2}{1+K_1([\overline{M}]+[\overline{L}])(1+K_2)}+k_{43}$
$k_{12}([\overline{M}]+[\overline{L}])$, k_{21}, k_{23}, $k_{32} \gtrsim k_{34}$, k_{43}	see Eqn. (25)	see Eqn. (26)	$k_{34}\frac{K_1([\overline{M}]+[\overline{L}])K_2}{1+K_1([\overline{M}]+[\overline{L}])(1+K_2)}+k_{43}$
$k_{12}([\overline{M}]+[\overline{L}])$, k_{21}, k_{34}, $k_{43} \gtrsim k_{23}$, k_{32}	$k_{12}([\overline{M}]+[\overline{L}])+k_{21}$	$k_{34}+k_{43}$	$k_{23}\frac{K_1([\overline{M}]+[\overline{L}])}{1+K_1([\overline{M}]+[\overline{L}])}+k_{32}\frac{1}{1+K_3}$

* $K_1 = k_{12}/k_{21}$, $K_2 = k_{23}/k_{32}$, $K_3 = k_{34}/k_{43}$.

IV. THE APPLICATION OF THE TEMPERATURE JUMP METHOD IN THE STUDY OF COMPLEX FORMATION

Studies of the kinetics of complex formation carried out in the early stages of the development of the chemistry of complex compounds made possible an arbitrary division into inert and labile complexes.[68,69] For inert complexes, substitution takes place in minutes or longer, whereas for labile complexes the half-reaction time is much less than one second.[69] A very large number of labile complexes, formed by the ions of the alkali, alkaline earth, and transition metals with various inorganic and organic ligands, are now known.[3,70–77] The study of labile complexes has become possible only with the development of methods for studying fast reactions, in particular the temperature jump method.

A large number of studies have been devoted to complex formation between a hydrated metal ion $M^{m+}(aq)$ and a unidentate ligand $L^{n-}(aq)$. The most general scheme for a reaction of this kind is given below:[63–64]

$$\underset{(X)}{M^{m+}(aq) + L^{n-}(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{(XI)}{M^{m+}(aq)\,(aq)\,L^{n-}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{(XII)}{M^{m+}(aq)L^{n-}} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{(XIII)}{ML^{(m-n)+}} \quad (41)$$

The initially solvated (hydrated) ions of the metal and the ligand, as a result of diffusion, form an encounter complex (XI), or an ion pair, in which the ions are separated from one another by not more than two monolayers of solvent molecules. The stage of ion pair formation is diffusion controlled, and therefore very fast. The rate constant k_{12} of the diffusion approach of the ions can be calculated from the expression[64,78]

$$k_{12} = \frac{4\pi Na}{1000}(D_+ + D_-)\left(\frac{\alpha}{e^\alpha - 1}\right)$$
$$\alpha = \frac{mne_0^2}{\varepsilon akT}\left(\frac{1}{1+\varkappa a}\right)$$
$$\varkappa = \left(\frac{8\pi e_0^2 NI}{1000\varepsilon kT}\right)^{1/2}$$

where D_+ and D_- are the diffusion coefficients of the cation and the anion, N Avogadro's number, a the distance of closest approach in the encounter complex; e_0 the charge of the electron, ε the dielectric constant of the medium, I the ionic strength, and k the Boltzmann constant.

The value of k_{12} for an encounter complex, for example with the 1:1 composition and $a = 0.7$ nm in an aqueous solution at $I = 0.01$ and 25 °C, is 1.1×10^{10} litre mole^{-1} s^{-1}.

The rate constant k_{21} for the diffusion separation of an encounter complex is given by the expression:[78,79]

$$k_{21} = \frac{3(D_+ + D_-)}{a^2}\frac{\alpha e^\alpha}{e^\alpha - 1}$$

The value of k_{21} for the same conditions is 6×10^9 s^{-1}.

The next stage (XI) ⇌ (XII) reflects the formation of the outer-sphere complex (XII), in which two ions are separated by only one monolayer of solvent molecules. Since the interaction between the ligand anion and the water molecule is weaker than that between the metal cation and the water molecule, the formation of the outer-sphere complex is accompanied by the loss of a water molecule from the hydration layer of the ligand. The stage (XI) ⇌ (XII) is also fast (k_{23}, $k_{32} \cong 10^8$–10^9 s^{-1}). The temperature jump method cannot distinguish stages (X) ⇌ (XI) and (XI) ⇌ (XII). Their existence follows from ultrasonic absorption data; three relaxation processes have been established for aqueous solutions of $CoSO_4$, $NiSO_4$, and $ZnSO_4$.[80]

The final stage (XII) ⇌ (XIII), that is the replacement of a water molecule from the inner coordination sphere of the metal ion by a molecule (ion) of the ligand, is the slowest stage, and gives the inner-sphere complex (XIII). Thus the stage (XII) ⇌ (XIII) is the limiting stage, and this makes it possible to simplify the reaction scheme (41) to the form given by scheme (21). The applicability of scheme (21) is confirmed by the experimental detection of two relaxation times. Thus the slow relaxation time is given by the expression

$$\tau^{-1} = K_1 k_{23}\frac{[\overline{M}]+[\overline{L}]}{1+K_1([\overline{M}]+[L])} + k_{32}$$

which can be used to find the value of k_{32} and the product $K_1.k_{23}$. The values of the product $K_1.k_{23}$ obtained in this way for complex formation by Ni^{2+} with various unidentate ligands ($CH_3PO_4^{2-}$, CH_3COO^-, NCS^-, F^-, HF, NH_3, C_5H_5N, etc.) have been published.[73] If K_1 is known, the rate constant for the formation of the inner-sphere complex k_{23} can also be determined.

The equilibrium constant K_1 can be estimated from the expression[81,82]

$$K_1 = \frac{4\pi Na^3}{3000}e^{-\alpha} \quad (42)$$

For some reactions, independent estimates of the values of K_1 have been obtained from spectral, polarometric, NMR, and EPR measurements.[69,74,83] These estimates show fairly good agreement with the values calculated from Eqn. (42) (see

Table 4), if it is assumed that $a = 4-5$ Å, as in the estimation of the distance of the closest approach in an encounter complex.[74]

Table 4. Values of the equilibrium constant K_1 for the formation of the outer-sphere complex in the system $M(aq)^{m+} + L(aq)^{n-}$.

System	K_1, litre mole^{-1}	
	calculation	experiment
$Ni(H_2O)_6^{2+} + CH_3PO_4^{2-}$	14 [69]	4 (Refs. 84, 85)
$Ni(H_2O)_6^{2+} + NH_3$	0.15 [69]	0.15 (Ref. 69)
$Ni(H_2O)_6^{2+} + CH_3COO^-$	3 [73]	—
$Ni(H_2O)_6^{2+} + C_5H_5N$	0.15 [73]	—
$Cr(H_2O)_6^{3+} + Cl^-$	13 [75]	—

Thus the temperature jump method and other methods for studying fast reactions can be used to find the values of the rate constants for the formation and dissociation of an inner-sphere complex.

1. Complex Formation With Unidentate Ligands

The extensive experimental material obtained in the study of the mechanism of fast reactions of complex formation has made it possible to separate the metals studied into three groups, depending on the magnitude of the rate constant of the inner-sphere replacement of a water molecule for different metal aquo-ions.[72] Fig. 2 gives characteristic values of the rate constants for this reaction. The first group consists of the alkali and alkaline earth metals (Ca^{2+}, Sr^{2+}, and Ba^{2+}). For the ions of these metals, the value of the rate constant for the exchange of coordinated water is greater than 10^7 s^{-1}.[86] In this case the limiting stage of the reaction is the attack by the ligand, and the observed reaction rate constant for complex formation is close to the diffusion value.

Table 5 gives the values of the rate constant of the replacement of coordinated water for the aquo-ions of the alkali metals, and shows that the rate of replacement depends on the nature of the ligand. The difference in the rates of substitution observed in each series can be explained simply by the difference in the electrostatic potentials (that is the charge/size ratios) of the metal ions.

The ions Zn^{2+}, Cd^{2+}, and Hg^{2+} react at the same high rates as Ca^{2+} (Fig. 2), but the rates do not depend significantly on the nature of the ligand. Thus for example for the Zn^{2+} ion the rate constant k_{23} for the replacement of water by SO_4^{2-} is 3×10^7 s^{-1},[87,88] and is close to the value 3.2×10^7 s^{-1} corresponding to complex formation by Zn^{2+} with oxalic acid.[71]

The second group contains the ions Fe^{3+}, Al^{3+}, and Be^{2+}, for which the rate of the exchange of a water molecule from the inner coordination sphere of the metal ion is lower than the rate of hydrolysis. The following mechanism of complex formation has been proposed for these ions. After the formation of the outer-sphere complex, hydrolysis takes place, followed by the formation of the inner-sphere complex, involving attack by a protonated ligand molecule:[78]

$$Fe^{3+}(aq) + L^-(aq) \rightleftharpoons (H_2O)_5Fe^{3+}(H_2O)L^- \rightleftharpoons$$
$$\rightleftharpoons (H_2O)_5FeOH^{2+}HL \rightleftharpoons (H_2O)_5FeL^{2+} + H_2O$$

According to this mechanism, the rate of complex formation depends on the nature of the ligand, and in particular on its basic strength. The mechanism of complex formation by Fe^{3+} with various ligands has been confirmed by the pressure jump method[89] and other methods for studying fast reactions.[90–92]

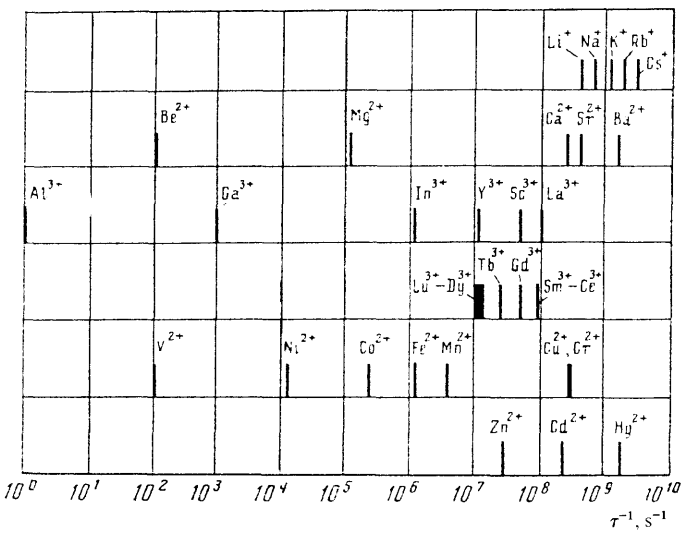


Figure 2. Characteristic rate constants (s^{-1}) of the inner-sphere replacement of a water molecule for various aquo-ions.[72]

Table 5. Values of the rate constants (10^{-7} τ^{-1}, s^{-1}) of substitution for alkali metal ions in water.[78]

Cation	$EDTA^{4-}$	NTA^{3-}	IDA^{2-}
Li^+	4.8	4.7	25
Na^+	4.7	8.8	25
K^+	7.5	15	—
Rb^+	14	23	—
Cs^+	21	35	—

Notation: NTA = nitrilotriacetate, IDA = iminodiacetate.

The third group consists of the ions of transition metals, and also metals of the main sub-groups of the periodic system, for which the rate constant for the exchange of coordinated water is less than 10^7 s^{-1}. A primary characteristic of these ions is that the rate constant for complex formation k_{eff} is practically independent of the nature of the ligand. Table 6 gives the values of k_{eff} obtained by the temperature jump method. A more complete summary of k_{eff} values obtained by other methods for studying fast reactions has been published.[74] The fact that k_{eff} is independent of the nature of the ligand is related to the fact that the limiting stage of the reaction is the removal of water molecules from the inner coordination sphere of the metal ion. The values of k_{eff} obtained experimentally and the values of K_1 calculated from Eqn. (42) can be used to determine k_{23}. For example, for complex formation by Ni^{2+} with CH_3COO^-, NH_3, and C_5H_5N,

$k_{23} = 3 \times 10^4$ s^{-1}.[73] On the other hand, the value of k_{23} practically coincides with the value of the rate constant for the exchange of coordinated water in metal aquo-ions.[74]

Table 6. Values of the rate constant k_{eff} for complex formation.

Metal ion	Ligand	lg k_{eff}, litre mole^{-1}s^{-1}	Refs.
Mg^{2+}	4,5-dihydroxybenzene-1,3-disulphonic acid	6.5	[93]
Mg^{2+}	8-quinolinol	5.5	[94]
V^{2+}	SCN^-	1.2	[95]
Fe^{2+}	SO_4^{2-}	3.6	[96]
Fe^{3+}	$Fe(CN)_6^{3-}$	3.2	[97]
Co^{2+}	SO_4^{2-}	5.3	[96]
Co^{2+}	NH_3	5.0	[98]
Co^{2+}	L-carnosine	5.6	[99]
Co^{2+}	α-alanine	5.8	[100]
Co^{2+}	β-alanine	4.8	[100]
Co^{2+}	4,5-dihydroxybenzene-1,3-disulphonic acid	6.0—6.6	[93]
Ni^{2+}	NH_3	3.2	[98]
Ni^{2+}	α-alanine	4.3	[100]
Ni^{2+}	α-aminobutyrate	4.0	[101]
Ni^{2+}	Murexide	3.5	[102]
$Ni(en)^{2+}$	NH_3	4.1	[103]
Cu^{2+}	L-carnosine	6.5	[104]
Cu^{2+}	Murexide	7.7	[105]
Zn^{2+}	Murexide	6.9	[105]
Cd^{2+}	pyridine-2-azodimethylaniline	7	[106]
Cd^{2+}	Murexide	8.1	[102]

Thus the results of kinetic measurements carried out chiefly by the temperature jump method, together with thermodynamic data (entropy and enthalpy of activation),[107] indicate that complex formation takes place by a dissociative mutual exchange mechanism (*Id* mechanism).[69,76] A large number of kinetic measurements have shown that the rate constant k_{23} depends markedly on the size and charge of the cation and other factors.[72] On the whole, the rate of replacement is lower, the greater the charge of the ion and the smaller its size. For example, the rate of complex formation by $Mg^{2+}(aq)$ with CrO_4^{2-}, ATP^{4-}, and ADP^{3-} is lower by 10^2—10^3 than that for $Ca^{2+}(aq)$.[72]

2. Complex Formation With Bidentate Ligands

The mechanism of complex formation by metal ions with bidentate ligands on the whole is analogous to the mechanism examined above for unidentate ligands. For bidentate ligands there is an additional stage of ring closure. The reaction scheme is given below:

$$\underset{\text{(XIV)}}{M^{m+}(aq) + L^{n-}(aq)} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{(XV)}}{M^{m+}(aq)L^{n-}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\text{(XVI)}}{M{-}L^{(m-n)+}} \underset{k_{43}}{\overset{k_{34}}{\rightleftharpoons}} \underset{\text{(XVII)}}{M{=}L^{(m-n)+}}$$

where the stages (XV) ⇌ (XVI) and (XVI) ⇌ (XVII) describe the formation of unidentate and bidentate inner-sphere complexes respectively. The last stage involves the replacement of a second water molecule from the inner coordination sphere of the metal ion and closure of the ring.

In complex formation involving a bidentate ligand, two cases are possible: 1) ring closure takes place at a higher rate than the formation of the encounter complex from the unidentate complex, that is $k_{34} \gg k_{32}$; this case corresponds to "normal" substitution;[73,100] 2) the stage of ring closure is slower, and is therefore the limiting stage in complex formation. These substitution reactions belong to the class of "sterically controlled" reactions.[100] The study of complex formation involving bidentate ligands by the temperature jump method has made it possible to observe two stages (two values of the relaxation time), corresponding to the replacement of two water molecules. Table 7 gives the values of the rate constants for different stages of complex formation by Ni^{2+} with various bidentate ligands.

Table 7. Rate constants for complex formation by Ni^{2+}.[73,108]

Aquo-ion	Ligand	K_1k_{23}, litre mole^{-1}s^{-1}	k_{32}, s^{-1}	k_{34}, s^{-1}	k_{43}, s^{-1}
$Ni(H_2O)_6^{2+}$	diaminoethylene	$4.0 \cdot 10^5$	$4.5 \cdot 10$	$9 \cdot 10^2$	$1.4 \cdot 10^{-1}$
$Ni(H_2O)_6^{2+}$	bipyridyl	$1.5 \cdot 10^3$	$4.5 \cdot 10$	$3 \cdot 10^3$	$3.4 \cdot 10^{-3}$
$Ni(H_2O)_6^{2+}$	maleate	$8.5 \cdot 10^5$	$3.5 \cdot 10^3$	$4.5 \cdot 10^3$	$1 \cdot 10^2$
$Ni(en)_2(H_2O)_6^{2+}$	diaminoethylene	$5.5 \cdot 10^6$	$1.2 \cdot 10^5$	$2.2 \cdot 10^5$	$8.7 \cdot 10$
$Ni(H_2O)_6^{2+}$	pyridine-2-azodimethyl-aniline	$1.5 \cdot 10^3$	$1.4 \cdot 10^4$	$2.9 \cdot 10^4$	$3 \cdot 10^{-1}$

An experimental criterion for distinguishing "normal" and "sterically controlled" substitution reactions is the magnitude of the volume of activation $\Delta V^{\neq}$.[109] Values of $\Delta V^{\neq}$ equal to 5—8 cm^3 mole^{-1} indicate that the reaction is a "normal" substitution reaction. For "sterically controlled" reactions, the values of $\Delta V^{\neq}$ are ~3 cm^3 mole^{-1}. The values of $\Delta V^{\neq}$ for complex formation by $Ni^{II}L$ with pyridine-2-azodimethylaniline (PAA) have been determined.[110] The measurements were made by the laser temperature jump method at pressures of up to 3 kbar. The reaction took place by the "normal" substitution mechanism when the ligand L was nitrilotriacetate, ethylenediaminediacetate, and diethylene-triamine, and by the "sterically controlled" reaction mechanism when L was 2,2',2''-triaminotriethylamine and triethylene-tetramine. The volumes of activation have also been determined for the reactions of Co^{II}, Cu^{II} and Zn^{II} with NH_3, PAA, glycinate, and Murexide.[77] In all cases the values of $\Delta V^{\neq}$ were positive, as is characteristic of the exchange-dissociative mechanism of complex formation.[17,109,111]

Convincing evidence in support of the "normal" substitution mechanism was obtained by complex formation by Ni^{2+} with PAA.[108,112] The laser photo-excitation method made it possible to observe directly the fast stage of five-membered ring closure.

In complex formation by Ni^{II} and Co^{II} with α-alanine, the limiting stage is the loss of the first water molecule from the inner coordination sphere of the metal ion, whereas for complex formation with β-alanine, the limiting stage is the ring closure.[113] The stage of ring closure probably also limits the rate of complex formation by the lanthanides of the cerium sub-group with the dye Xylenol Orange.[114] The values of the reaction rate constants given in Ref.114 are appreciably lower than the rate constants for the exchange of water in lanthanide ions.[74] It is suggested that the low rate of formation of the chelate compound compared with the rate of formation of the unidentate inner-sphere complex is related to the difficulty of the formation of six- and seven-membered chelate compounds.

Complex formation in micellar solutions has been studied.[115,116] For the reaction of Ni^{II} with PAA in the presence of sodium dodecylsulphate, the maximum reaction rate is achieved close to the critical micelle concentration, and the reaction takes place by an Id mechanism.

The ions of transition metals and other multivalent cations can form complexes with more than one ligand. On the whole, the rate of complex formation by a metal with a second and subsequent ligands is greater than that with the first ligand. Since the ligands are generally stronger electron donors than the water molecule, it follows that on complex formation with the first ligand, the effective charge of the metal cation is decreased, and the radius increases, and there is an overall increase in the exchange rate.[74]

The study of the kinetics of complex formation in non-aqueous media has established that reactions with unidentate ligands take place by an *Id* mechanism. For bidentate ligands, the organic solvent has a specific influence,[107] in that complex formation is either slower or faster than normal substitution in aqueous solutions. The study of the role of the solvent has shown that for bidentate ligands, for which in the case of the normal substitution reaction in water the relationship $k_{eff} = K_1k_{23}$ applies, the ratio k_{eff}/K_1k_{23} deviates considerably from unity. This deviation is due to the influence of the solvent on all three stages of complex formation represented by scheme (43). The nature of the solvent influences the stability of the outer-sphere complex and the orientation of the ligand in the outer sphere.[77] These factors are also influenced by ion–dipole interaction and the formation of H-bonds.[117] For example, the mechanism of the formation of $BeSO_4$ in a water–dimethyl sulphoxide mixture is much more complex than that in aqueous solution,[118] as indicated by the experimental observation of five values of the relaxation times.

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Thus the temperature jump method has proved to be extremely promising for the study of the kinetics and mechanism of complex formation. The further development of experimental technique should create the conditions for the development of this method and its extensive introduction in the study of various types of chemical transformation, and the temperature jump method will occupy an important place among other physical methods for studying fast reactions.

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Vernadskii Institute of
Geochemistry and Analytical
Chemistry, Moscow.

Translated from *Uspekhi Khimii*, 53, 1625-1647 (1984) U.D.C. 547.638 + 547.556.7

The Development and Synthetic Applications of the Meerwein Reaction

A.V.Dombrovskii

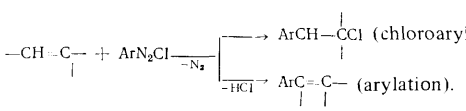
The development of the study of the Meerwein reaction is described and the reactions involving the anion-arylation and arylation of unsaturated compounds by aromatic diazo-compounds and catalysed by transition metal salts are examined and surveyed. The modern ideas about the mechanisms of these reactions and the possibility of their employment in organic synthesis are discussed.
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I. INTRODUCTION

Meerwein[1] described in 1939 the copper(II) chloride-catalysed reaction of unsaturated compounds with arenediazonium chlorides (ADC), which results in the elimination of the nitrogen of the diazo-group and the hydrogen attached to the sp^2-carbon atom is substituted by the aryl group or the aryl group and the chlorine atom add to the multiple bond. Subsequently these reactions were called arylation and chloroarylation respectively:[2]



The Meerwein reaction proved to be an extremely valuable synthetic method whereby it is possible to obtain aliphatic-aromatic olefins and polyfunctional compounds in a single step at low temperatures from a very large number of readily available, cheap, unsaturated compounds and aromatic amines. The olefins can be used in their turn in many reactions in organic synthesis to obtain substances of practical interest.

The subsequent development of this reaction involved the improvement of methods and expansion of the range of saturated and aromatic diazo-compounds employed, containing the anions Cl^-, Br^-, CN^-, HO^-, BF_4^-, $MeCOO^-$, SO_4H^-, NO_3^-, etc. Chloroarylation can be regarded as a special (albeit the commonest) case of the general reaction involving the anion-arylation of unsaturated compounds by aromatic diazo-compounds. Subsequently, it was found that, apart from $CuCl_2$, the reaction is catalysed by CuCl and other salts, mainly transition metal halides.

Since the discovery of the Meerwein reaction, several hundreds of publications, both experimental and theoretical, concerning chloroarylation and arylation of unsaturated compounds have appeared, mainly in the Soviety Union. The first survey of the reactions of unsaturated compounds with aromatic diazo-compounds was published by the present author.[3] Subsequently other reviews appeared,[4-6] covering the literature mainly up to 1970, in which the results obtained were not fully described. This review suggests and surveys the literature data up to 1983. The results of earlier studies are quoted only in so far as it is necessary.

II. THE REACTION MECHANISM

The mechanism of the Meerwein reaction has been discussed for a long time. It was not clear whether the reaction is of the ionic or radical type. The question of what is in actual fact the catalyst, $CuCl_2$ or CuCl, has been controversial; in the absence of these salts, neither chloroarylation nor arylation occurs in most cases. There was a need for theoretical and experimental explanations of a number of side reactions and products accompanying the chloroarylation and arylation reactions. Different versions of the mechanism of this reaction, based on theoretical and experimental studies performed with different degrees of scientific expertise, have been proposed at different times. The polar mechanism proposed by Meerwein[1] and other investigators[2-4] proved unacceptable for a number of reasons. In both early and later studies the majority of investigators of this reaction concluded that, like the Sandmeyer reaction, the Meerwein reaction is catalysed by copper(I) halides and has a radical mechanism.[7,8]

The Meerwein reaction should probably be regarded as an extended version of the Sandmeyer reaction, which in this case occurs in the presence of an unsaturated compound. In the Sandmeyer reaction the aryl radicals and halogen atoms combine to form aryl halides. On the other hand, in the presence of an unsaturated compound, these species interact with the multiple bonds to form chloroarylation and arylation products. The involvement of the molecules of the unsaturated compound, interacting with the arenediazonium ion and the catalyst, apparently leads to the appearance of a ternary reaction complex in the simplest case,[9] which in its turn modifies the mechanism of the entire process.

It is known that transition metal halides, including copper-halides, react with arenediazonium chlorides to form complexes (double salts),[10-14] which are relatively stable in aqueous organic solutions in the cold and at room temperature but begin to decompose after the addition of an unsaturated compound. It has been demonstrated by ultraviolet and infrared spectroscopy[15] that there is a chemical bond between the metal ions and the nitrogen of the diazo-group in double salts of this kind. On the other hand, it is known that copper(I) halides form π-complexes with many olefins even in an aqueous medium. Such complexes react with the ADC to form the product of the Meerwein reaction. The stability of the complexes diminishes in the sequence CuCl > CuBr > CuI; the cyanide CuCN does not form complexes and does not catalyse the Meerwein reaction.[16] The Meerwein reaction and

the catalytic effect of copper halide on the latter should therefore be regarded as radical oxidation-reduction addition to olefins[17] whose mechanism includes a series of consecutive elementary reactions leading to the main and side products. The most logical and experimentally demonstrated mechanism of the interaction of the ADC–copper chloride–unsaturated compound system has been proposed by Schrauzer[18] [reactions (1)–(8)].

Under the classical conditions of the Meerwein reaction, an aqueous acetone solution of $CuCl_2$, whose reduction by acetone to CuCl is well known[19] [reaction (1)], is used. The CuCl generated at the instant of reaction is apparently more reactive than the preparation obtained beforehand. The CuCl formed during the reaction or introduced as such forms a double salt with the ADC [reaction (2)], in which the diazo-group is coordinated to the complex anion $CuCl_2^-$; such complexes are known for transition metal chlorides.[20] The double salt then forms a ternary reaction complex with the olefin (–CH=C<), in which the diazo-group and the olefin are linked to the copper ion in conformity with the coordination number, which is two [reaction (3)]. The details of the binding and of the geometry of the species within the ternary complex are so far unknown.

The onset of reaction is signalled by the evolution of nitrogen (as a result of its elimination from the diazo-group), which begins only after the addition of the olefin. Under the influence of the polarising action of the copper ion and the olefin, the arenediazonium cation is reduced to the radical Ar·. The electrochemical reduction of arenediazonium salts at copper, iron, and other metal cathodes in the presence of unsaturated compounds has demonstrated[21] that this involves the generation of aryl radicals, which interact with the π-bond of the olefin. In this case the diazonium cation is initially reduced via a one-electron mechanism to the arenediazonium radical, which then decomposes to the radical Ar· and free nitrogen:[21–23]

$$[PhN_2]^+ + e \rightarrow PhN_2^{\cdot} \rightarrow Ph^{\cdot} + N_2 .$$

Without being released into the bulk of the medium, the radical Ar· reacts with the olefin to form an aliphatic-aromatic radical [reaction (4)] whose interaction with $CuCl_2$ entails the formation of the chloroarylation product as a consequence of the transfer of the radical species Cl· [reaction (5)]. If there is a hydrogen atom at the α-carbon atom in the aliphatic component of the aliphatic-aromatic radicals, the latter can be eliminated together with a chlorine atom in the form of HCl [reaction (5a)], which constitutes one of the interpretations of the arylation mechanism.[6] One cannot rule out the possibility that the hydrogen atom in the olefin or another ligand can be substituted by the radical Ar· directly:

$$2CuCl_2 + Me_2CO \rightarrow 2CuCl + MeCOCH_2Cl + HCl , \quad (1)$$

$$ArN_2^+Cl^- + CuCl \rightleftarrows ArN_2^+CuCl_2^- , \quad (2)$$

$$ArN_2^+CuCl_2^- \underset{\leftarrow}{\overset{-HC\equiv C<}{\rightarrow}} \left[ArN_2^+CuCl_2^- \cdot \begin{matrix} -C- \\ \| \\ -CH \end{matrix} \right] , \quad (3)$$

$$\left[ArN_2^+CuCl_2^- \cdot \begin{matrix} -C- \\ \| \\ -CH \end{matrix} \right] \xrightarrow{-N_2} [ArCH-\dot{C}-\cdots Cu^{\cdot}Cl_2] , \quad (4)$$

$$[ArCH-\dot{C}-\cdots Cu^{\cdot}Cl_2] \xrightarrow{-CuCl} \begin{cases} \rightarrow ArCH-C(Cl)- , & (5) \\ \xrightarrow{-HCl} ArC(=)C- , & (5a) \end{cases}$$

$$Ar^{\cdot} + Cu^{\cdot}Cl_2 \rightarrow ArCl + CuCl , \quad (6)$$

$$Ar^{\cdot} + Me_2CO \rightarrow ArH + MeCO\dot{C}H_2 , \quad (7)$$

$$ArN_2Cl + H_2O \rightarrow ArOH + HCl + N_2 , \quad (8)$$

$$ArCH-\dot{C}H-\cdots CuCl_2 \xrightarrow[-CuCl]{-HC\equiv C-} Ar(CH=\dot{C}-)_2Cl , \quad (9)$$

$$2ArC(\cdot)-\dot{C}- \rightarrow \left(ArC(-)-C- \right)_2 . \quad (10)$$

Thus, under the conditions of "cuprocatalysis", the chloroarylation proceeds as a redox-initiated free radical addition via stage involving the formation of intermediate complexes of the catalyst with the diazo-compound and with the unsaturated compound.

If for any reason the radical species Ar· and Cl· leave the inner sphere of the reaction complex, side reactions take place, in the first place the formation of ArCl (the Sandmeyer reaction), aromatic hydrocarbons and phenols reaction (6)–(8). The Meerwein reaction is also accompanied by the formation of resins, telomers, and additive dimers. The telomers are formed if the aliphatic-aromatic radical reacts with the next molecule of the monomeric olefin and then the $CuCl_2$ radical [reaction (9)]. As in the polymerisation of unsaturated compounds in the presence of variable-valence catalysts, telomers appear in this instance and under certain conditions can be the main reaction products.[24–29] Additive dimers arise as a consequence of the recombination of the same aliphatic-aromatic radicals [reaction (10)].[30,31]

Arylation formally involves the substitution of a hydrogen atom at a carbon atom involved in the multiple bond by the aryl group of the diazo-compound. Arylation should apparently be regarded in most cases as an addition–elimination process, which can be demonstrated by purely chemical means. It has been shown[32] that, on interaction with the ADC, α-chlorostyrene gives rise smoothly and in satisfactory yields to the α-chlorostilbenes PhCCl=CHAr (Ar = Ph, 4-MeC_6H_4, or 4-$O_2NC_6H_4$). If α-bromostyrene is used in the reaction, then the same α-chlorostilbenes are obtained in virtually quantitative yields:[33]

$$PhCBr=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} [PhCBrCl-CH_2Ar] \xrightarrow[-HBr]{} PhCCl=CHAr .$$

Consequently, the arylation of α-halogenostyrenes proceeds via a stage involving the addition of the Ar group and the Cl atom of the arenediazonium cation to the ethylenic bond. Since the C–Cl bond in the adduct obtained from α-bromostyrene is stronger than the C–Br bond, HBr and HCl are split off on spontaneous decomposition of the unstable intermediate adduct and α-chlorostilbene is obtained as a result.

III. FACTORS DETERMINING THE EFFECTIVENESS OF THE REACTION

The effectiveness of the reaction, i.e. the yields of the chloroarylation and arylation products, depends on a series of factors, the most important of which are as follows.

The unsaturated component (olefin). The vinyl monomers $H_2C=CH-X$ and $H_2C=CX_2$, in which the ethylenic bond has been activated by one or two electron-accepting groups (X = Cl, CN, Ar, $-C=CH_2$, COR, COOH, COOAlk, etc.) usually react satisfactorily. Because copper halides are capable of transferring radical chains very effectively, such monomers do not give rise to high-molecular-weight compounds. Ethylene, acetylene, and their substituted derivatives, containing electron-donating groups, react poorly. The unsaturated compounds RHC=CHR in which the double bond has been blocked also react with difficulty.

The arenediazonium component. ADC (concentrated or even saturated aqueous solutions are used for the reaction), which are capable of forming complexes with copper halides,

give the best results in most cases. Arenediazonium salts containing other anions usually give rise to lower yields of chloroarylation and arylation products.

The best yields of products are obtained when the *para*-position in the aromatic ring contains a substituent, regardless of the electronic effect which it exhibits; *ortho*- and *meta*-substituted derivatives give rise to lower yields.

Apart from arenediazonium salts (including tetrafluoroborates[34,35]), other compounds forming aryl radicals, for example, benzoyl peroxide, arylhydrazone peroxides, 1-aryl-3,3-dimethyltriazenes, *N*-nitrosoacetanilides, diazoaminobenzene, and diaryliodonium salts, have been proposed for the arylation of olefins;[6] aryl radicals generated by the electrochemical reduction of diazonium salts have also been used.[21] However, with the exception of arylpalladium reagents,[36,37] such sources of aryl radicals have given lower yields of arylation products and in most cases initiated the polymerisation of the olefins.[6]

Catalysts. Apart from copper halides, the salts $FeCl_2$,[30,31,38] $HgCl_2$,[39] $LiPdCl_3$,[40] and Pd(0) (obtained *in situ*)[41] and the $CuSO_4 + FeSO_4$, $Cu(NO_3)_2 + Cu$, and $Cu(NO_3)_2 + Fe$ systems[30] have been used for chloroarylation and arylation. However, $CuCl_2$ and CuCl, used in an amount equivalent to 10–20 mole % per mole of the ADC, still remain the best catalysts. An increase of the catalyst concentration promotes the occurrence of the Sandmeyer reaction, while at lower concentrations ArH is formed.[2,6]

The catalytic capacity of copper halides, iron(II) salts, and certain other redox initiators, can be explained by the comparatively low oxidation-reduction potentials E of the ions of these metals; for example, $E = 0.16$ eV for the $Cu^+ \rightarrow Cu^{2+}$ system and $E = 0.77$ eV for $Fe^{2+} \rightarrow Fe^{3+}$.

The potentials E for the metal ions in the salts $FeCl_3$, $AlCl_3$, $ZnCl_2$, $CdCl_2$, $CoCl_2$, $MnCl_2$, and $NiCl_2$, which do not catalyse or only weakly catalyse chloroarylation and arylation, are significantly higher.[31] Cases are known where arylation takes place in the absence of catalysts, for example, in the reactions of arenediazonium salts with coumarin,[1] quinones, and ferrocene,[2] which can be accounted for by the fairly low oxidation-reduction potentials of these compounds.[31]

Solvents. The chloroarylation and arylation reactions usually take place in aqueous organic media with vigorous stirring. In the absence of water, the reactions hardly begin. In those cases where the arenediazonium and olefinic components dissolve in water, the reactions have been achieved successfully in aqueous media.[2,6] The nature of the organic solvent has a significant influence on the effectiveness of the reaction. The most important requirement which this organic solvent must meet is that it is miscible with water without binding the catalyst chemically at the same time. Solvents such as tetrahydrofuran (THF), 1,4-dioxan, ether, dimethylformamide (DMF), dimethyl sulphoxide (DMSO), and pyridine, which apparently bind copper halides and other catalysts in complexes removing them from the reaction sphere thereby, proved to be ineffective.[2,6,42]

Acetone, acetonitrile, and sulpholan proved to be the most suitable solvents. A water–acetone mixture, the volume ratios of the components of which are varied in the range 3 : 1–7 : 10, is usually employed for the reactions.

The pH of the medium. Media close to neutrality (pH 4–6) are optimal in reactions with arenediazonium salts containing electron-donating substituents in the aromatic ring. In the presence of electron-accepting substituents in the ring a high acidity of the medium is required (pH 1–2). It has been suggested that MeCOONa, CaO, $Ca(OH)_2$, and $NaHCO_3$ be added to the reaction mixture in order to maintain and regulate the necessary pH.[2]

Temperature. The chloroarylation and arylation reactions proceed under mild conditions as regards temperature (from −5 to +30 °C). In a few instances the evolution of nitrogen begins at −10 °C. If the temperature is not regulated, then the interaction becomes vigorous, the temperature rises rapidly, and nitrogen is evolved in abundance; in such cases the Sandmeyer reaction and resin formation predominate.

IV. THE LATEST DATA ON THE MEERWEIN REACTION

Studies devoted to the reactions of olefins and their derivatives with arenediazonium salts, which have not been included in previous reviews,[2,3,6] are discussed below. In a number of instances the applications of the products of the anion-arylation and arylation reactions in organic synthesis are indicated.

1. Alkenes, Halogenoalkenes, and Certain Vinyl Monomers

The simplest alkenes, namely ethylene and propene, react with difficulty even with the most reactive ADC. Only under comparatively severe conditions in an autoclave, does ethylene react with diazotised 4-nitroaniline to form 1-chloro-2-(4-nitrophenyl)ethane (45–50%),[43] which is quantitatively converted into 4-nitrostyrene on dehydrochlorination:[2]

$$H_2C{=}CH_2 + 4\text{-}O_2NC_6H_4N_2Cl \xrightarrow[42^\circ C;\ 70\text{–}75\ atm\ N_2]{CuCl_2} \rightarrow 4\text{-}O_2NC_6H_4CH_2CH_2Cl \xrightarrow[-NaCl]{NaOH} 4\text{-}O_2NC_6H_4CH{=}CH_2 .$$

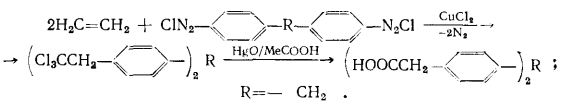
Halogenoalkenes with halogen atoms attached to the sp^2-carbon atom give rise to chloroarylation products on interaction with ADC; the mode of addition to the multiple bond is then consistent with the Markovnikov rule. The vinyl chloride gives rise to 1,1-dichloro-2-arylethanes (60–70%),[44–46] which have served as starting materials for the synthesis of 4-nitrophenylacetaldehyde,[47] β-chlorostyrenes,[48] 1,4-bis-(β-chlorovinyl)benzene, and 1,3-dioxolan-4-ylphenylenediacetaldehyde:[46]

$$H_2C{=}CHCl + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CHCl_2 ;$$
$$Ar{=}Ph,\ 4\text{-}MeC_6H_4,\ 4\text{-}MeOC_6H_4,\ 4\text{-}BrC_6H_4,$$
$$2,4\text{-}Cl_2C_6H_3,\ 4\text{-}O_2NC_6H_4 .$$

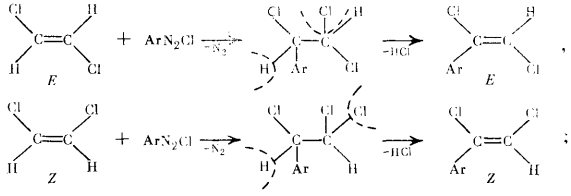
Vinylidene chloride reacts particularly effectively with ADC to form 2,2,2-trichloroarylethanes (~80%),[49] which proved to be convenient starting materials for the synthesis of arylacetic acids[50] and 1,4-bis(ββ-dichlorovinyl)benzene:[51]

$$H_2C{=}CCl_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CCl_3 ;$$
$$Ar\text{-}4\text{-}MeC_6H_4,\ 4\text{-}ClC_6H_4,\ 4\text{-}MeOC_6H_4,$$
$$4\text{-}O_2NC_6H_4,\ 4\text{-}Cl_3CH_2C_6H_4 .$$

Biphenyl-4,4′-bisdiazonium chloride reacts via both diazo-groups with two molecules of vinylidene chloride to form 4,4′-bis(2,2,2-trichloroethyl)biphenyl (30%), which is converted into biphenyl-4,4′-diacetic acid after hydrolysis. Vinylidene chloride reacts analogously with tetrazonium chloride containing a bridging group between the benzene rings:[52]



The symmetrical dichloroethylene reacts poorly with ADC. The reactivity of the *E*-isomer is twice as high as that of the *Z*-isomer. The reaction results in the formation of 2-aryl-1,1,2-trichloroethanes (two conformers), which are converted into the *E*- and *Z*-aryl-1,2-dichloroethylenes on alkaline dehydrochlorination. HCl is eliminated as a result of the abstraction of the α-hydrogen atom and the chlorine atom from the transoid β-position:[53]



Ar = Ph, 4-ClC_6H_4.

1,3-Dichlorobut-2-ene reacts with benzenediazonium chloride to form $MeCCl_2CH(Ph)CH_2Cl$ in a low yield (~30%),[54] while trichloroethylene gives rise to moderate yields (~50%) of aryl-1,1,1,2-tetrachloroethanes, which are smoothly dehydrochlorinated by an alcoholic solution of alkali to give α,β,β-trichlorostyrenes:[55]

$$ClHC{=}CCl_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCHClCCl_3 \xrightarrow[-HCl]{KOH} ArCCl{=}CCl_2;$$
Ar = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-$O_2NC_6H_4$

Fluorine-containing olefins react with ADC in the usual way, forming adducts, which are converted on dehydrochlorination into the corresponding fluorine-containing aryl derivatives,[56] for example:

$$F_2CHCF_2CH{=}CH_2 + 4\text{-}RC_6H_4N_2Cl \xrightarrow[N_2]{CuCl_2,\ 33^\circ C} \rightarrow$$
$$\rightarrow F_2CHCF_2CHClCH_2C_6H_4R\text{-}4 \xrightarrow[-KCl,\ -H_2O]{KOH/MeOH} F_2CHCF_2CH{=}CHC_6H_4\text{-}R\text{-}4;$$
R = Cl, NO_2, COOH (28—50%).

$F_2CHCF_2C(Me){=}CH_2$, $F_2CH(CF_2)_3CF{=}CF_2$, $CF_3(CF_2)_4CF{=}CF_2$, and $C_4H_9CF{=}CFCl$ react analogously; chlorotrifluoroethylene gives rise to the adducts $ArCF_2CFCl$ (27%) only under comparatively severe conditions (40–50 °C, in an autoclave), while $H_2C{=}CF_2$ and $F_2C{=}CF_2$ hardly react even with the most reactive ADC.[56]

1,1,1-Trifluoropropene reacts with 4-nitrobenzenediazonium halides to form adducts (yield 30–40%), which are also readily dehydrohalogenated and give almost quantitative yields of 2-(4-nitrophenyl)-1-trifluoromethylethylenes:[57]

$$F_3CCH{=}CH_2 + ArN_2X \xrightarrow[MeCOONa]{CaX_2,} F_3CCHXCH_2Ar \xrightarrow[-HCl]{Et_3N} F_3CCH{=}CHAr;$$
Ar = 4-$O_2NC_6H_4$; X = Cl, Br.

The reactions of ADC (catalysed by $CuCl_2$) with vinylsilanes, vinylphosphonate, and vinyl sulphones also involve the addition of chlorine and the aryl groups in the α- and β-positions respectively to the vinyl component. Vinylsilane $Ph_3SiCH{=}CH_2$ gives rise to 15–37% yields of the compounds $Ph_3SiCHClCH_2Ar$ (Ar = 4-ClC_6H_4, 4-BrC_6H_4, 4-$HOCOC_6H_4$, or 3- and 4-$O_2NC_6H_4$);[2] the reactions of $(EtO)_2P(O)CH{=}CH_2$ result in 45% yields of the compounds $(EtO)_2P(O)CHClCH_2Ar$ (Ar = Ph or 4-ClC_6H_4).[58]

Vinyl sulphones react analogously with ADC to form β-aryl-α-halogenoethyl sulphones (yields up to 45%), which are converted on dehydrochlorination into styryl sulphones in high yields:[59–61]

$$RSO_2CH{=}CH_2 \xrightarrow[-N_2]{ArN_2X,\ CuCl_2} RSO_2CHXCH_2Ar \xrightarrow[HX]{base} RSO_2CH{=}CHAr;$$
R = Me, Et, CF_3, 4-MeC_6H_4; X = Cl, Br;
Ar = Ph, 4-FC_6H_4, 4-ClC_6H_4, 3- and 4-$O_2NC_6H_4$, 4-$HOCOC_6H_4$.

2. Acetylenes

The C≡C bond is less reactive in the reactions with ADC than the C=C bond. Like ethylene, acetylene itself undergoes the Meerwein reaction with 4-nitrobenzenediazonium chloride to form a low yield (~20%) of the chloroarylation product, which is wholly dehydrochlorinated by an alcoholic solution of alkali and is converted into 4-nitrophenylacetylene. Substituted acetylenes are more reactive. Thus phenylacetylene is chloroarylated to α-chlorostilbenes in satisfactory yields (46–70%) and the latter have been converted on dehydrochlorination into tolanes (yield 85%):[2]

$$R{-}C{\equiv}CH + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} R{-}CCl{=}CH{-}Ar \xrightarrow[-HCl]{KOH/\ dioxan} R{-}C{\equiv}C{-}Ar;$$
R = H, Ph; Ar = Ph, 4-$O_2NC_6H_4$.

Vinyl- and isopropenylacetylenes react with ADC via the ethylenic bond to form chloroarylbutynes, which are converted into arylbutenynes on dehydrochlorination. Allene derivatives have been detected in small amounts together with the chloroaryl derivatives:[62–64]

$$H_2C{=}CR{-}C{\equiv}CH + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CCl(R){-}C{\equiv}CH \xrightarrow[-HCl]{KOH} \rightarrow$$
$$\rightarrow ArCH{=}CR{-}C{\equiv}CH;$$
R = H, Me; Ar = Ph, 4-ClC_6H_4, 4-$MeOC_6H_4$.

Tetrazonium chloridee based on 4,4′-diaminobiphenyl, 4,4′-diamino-3,3′-dimethoxybiphenyl, di(4-aminophenyl) sulphone, and di(4-aminophenyl) ether react via the acetylenic bond with propargyl alcohol, propargylic acid, and phenylacetylene (in the presence of CuCl as the catalyst) with evolution of nitrogen from both diazo-groups, forming bischloroarylation products (46–58%):[65]

$$2HC{\equiv}CR + R''[{-}C_6H_3(R')N_2Cl]_2 \xrightarrow[2N_2]{CuCl_2} [{-}C_6H_3(R')CH{=}CClR]_2R'';$$
R = MeO, COOH, Ph; R′ = H, MeO;
R″ = —, CH_2, SO_2, O.

3. Arylethylenes

Arylethylenes in which the aryl group is conjugated with the ethylenic bond have been widely used in the anion-arylation and arylation reactions. Arylethylenes with a terminal $>C{=}CH_2$ group exhibit an enhanced reactivity. Apart from the electronic effects, steric factors have an effect in this case.

Styrene reacts with ADC at pH ~ 5 ($CuCl_2$, aqueous acetone solution of MeCOONa) to form stilbenes;[2] however, in an acidic medium (pH 1–2) chloroarylation takes place and 2-aryl-1-chloro-1-phenylethanes are formed in satisfactory yields and are readily dehydrochlorinated and converted almost quantitatively into substituted stilbenes:[66–68]

$$PhHC{=}CH_2 + ArN_2Cl \xrightarrow[-N_2]{\begin{cases} \xrightarrow[-HCl]{pH\sim5} PhHC{=}CHAr, & (a) \\ \xrightarrow{pH\ 1\text{-}2} PhHCClCH_2Ar \xrightarrow[-HX]{base} PhHC{=}CHAr; & (b) \end{cases}}$$
(a) Ar-4-ClC_6H_4, 4-$MeOC_6H_4$;
(b) Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, 4-$EtOCOC_6H_4$, 4-$Et_2NC_2H_4OCOC_6H_4$, 2-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$.

Arylethylenes containing electron-donating substituents in the aromatic ring or at the ethylenic bond are as a rule readily arylated. The reaction is one of the practically convenient methods of synthesis of substituted stilbenes, frequently in high yields; examples are presented below (the yields expressed as percentages are indicated in brackets):

$$RR^1C{=}CHR^2 + ArN_2Cl \xrightarrow{-N_2} RR^1C{-}CR^2Ar + HCl;$$

R = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$; R^1 = H, Me, F, Cl, Ph; R^2 = H, Et; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$, 4-$HOCOC_6H_4$, 4-$MeOC_6H_4$, 4-NCC_6H_4, 4-$MeCOC_6H_4$, 4-$HOSO_2C_6H_4$, 4-$H_2NSO_2C_6H_4$, 4-$Et_2NC_2H_4C_6H_4$, 4-$Et_2NC_2H_4OCOC_6H_4$ [2, 33, 68, 69]

Styrene enters into the copper salt-catalysed anion-arylation reaction with benzenediazonium salts in the presence of sodium nitrite or sulphide:[70]

$$PhHC{=}CH_2 \xrightarrow[-N_2]{PhN_2Cl,\ CuCl_2} \begin{cases} \xrightarrow{NaNO_2} PhCH(NO_2)CH_2Ph & (20\%), \\ \xrightarrow{Na_2S} (PhCH_2CHPh)_2S & (25\%). \end{cases}$$

Anion-arylation of styrenes. Styrene reacts with arenediazonium sulphates in an acetic acid–acetone solution saturated with sulphur(IV) oxide in the presence of thiocyanate anions and copper(I) thiocyanate. It is assumed that arenediazonium thiocyanates are formed in the reaction and then generate Ar$^{\cdot}$ radicals. The latter react with SO_2 to form arenesulphonyl radicals, which add together with thiocyanate radicals to the ethyleneic bond of styrene. This results in the formation of 2-(arenesulphonyl)-1-phenyl-1-thiocyanatoethanes (in ~60% yields):[47]

$$ArN_2SO_4H + NH_4SCN \rightleftarrows ArN_2SCN + NH_4HSO_4,$$

$$ArN_2SCN \xrightarrow[-N_2]{SO_2,\ CuSCN} [ArSO_2^{\cdot} + {\cdot}SCN] \xrightarrow{PhHC{=}CH_2} PhHC(SCN)CH_2SO_2Ar;$$

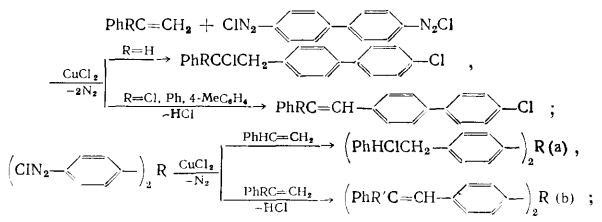
Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 4-$O_2NC_6H_4$.

Under analogous conditions but in the presence of chloride, bromide, *O,O*-diethyl phosphorodithioate, or xanthate anions and catalytic amounts of copper ions, styrene reacts with aromatic diazo-compounds, forming crystalline anion-sulphonylation products (in yields of ~80%): 2-(arenesulphonyl)-1-chloro-1-phenylethanes, 2-(arenesulphonyl)-1-bromo-1-phenylethanes, 2-(arenesulphonyl)-1-(*O,O*-diethylphosphorodithioato)-1-phenylethanes, and 2-(arenesulphonyl)-1-(*O*-ethyl dithiocarbonato)-1-phenylethanes:[48]

$$PhHC{=}CH_2 + ArN_2X + SO_2 + MHal \xrightarrow{CuHal} PhHC(Hal)CH_2SO_2Ar;$$

X = Cl, Br, SO_4H; M = Na, K; Hal = Cl, Br, $(EtO)_2PS_2$, EtOC(S)S; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$.

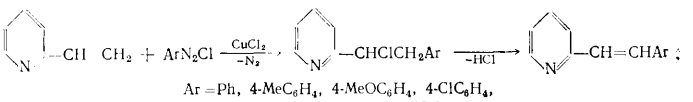
Styrene reacts with biphenyl-4,4'-bisdiazonium chloride with evolution of nitrogen from both diazo-groups, one of which undergoes the Sandmeyer reaction, while the other chloroarylates one styrene molecule to form 4-chloro-4'-(2-chloro-2-phenylethyl)biphenyl in 57% yield. α-Substituted styrenes (R = Ph, Cl or 4-MeC_6H_4) gives rise to products of arylation involving one diazo-group, while the other diazo-group is substituted by chlorine (yields ~50%):[52]



(a) R = S (40), CH_2 (67);
(b) R = S; R' = Cl (33), Ph (49); R = CH_2; R' = Cl (54), Ph (49).

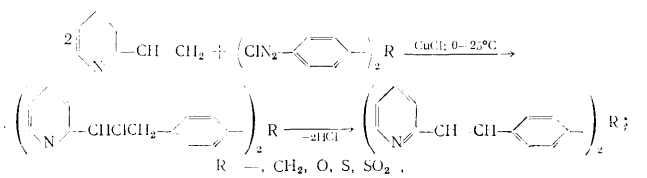
It has been stated[71] that styrene is arylated by bisdiazotised benzidine to form 4,4'-distyrylbiphenyl (yield 14%). Tetrazonium chlorides with a bridging S atom or CH_2 group between the benzene rings react with styrene via both diazo-groups. In reaction (a) the diazo-groups of di(4-diazoniaphenyl)-sulphide chloride and di(4-diazoniaphenyl)methane chloride react with two molecules of styrene to form chloroarylation products. In reaction (b) α-substituted styrenes react with the same tetrazonium chlorides to form arylation products[52] (the yields expressed as percentages are given in brackets). Numerous biphenyl, diphenyl sulphide, and diphenylmethylene derivatives have been synthesised from compounds obtained by chloroarylating and arylating various styrenes by tetrazonium chlorides.[52]

Like styrene, 2-vinylpyridine reacts with ADC to form 2-aryl-1-chloro-1-(2'-pyridyl)ethanes (in 50–60% yields), which are readily converted into 2-stilbazoles on dehydrochlorination (80–96%):[72]



Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-BrC_6H_4, 2-$O_2NC_6H_4$, 4-$O_2NC_6H_4$.

2-Vinylpyridine is also readily chloroarylated by tetrazonium chlorides, giving rise to bisadducts, which are converted into bis-stilbazoles (in 80% yield) on treatment with an alcoholic solution of alkali:[73]



R = —, CH_2, O, S, SO_2.

4. Conjugated Dienes

Conjugated dienes react extremely vigorously with aromatic diazo-compounds, evolving nitrogen from the diazo-group and giving rise to arylation, chloroarylation, and anion-arylation products, which are formed readily when the reaction is catalysed by both $CuCl_2$ and CuCl.

In order to explain the mechanism of the chloroarylation of conjugated dienes, it has been assumed,[8] on the basis of data obtained from conductimetric measurements in the ArN_2Cl–CuCl-buta-1,4-diene system, that the chlorine atom in the double salt of arenediazonium and copper(I) chlorides is substituted by the diene. The resulting ternary complex decomposes with evolution of nitrogen from the diazo-group as a consequence of a redox process within the complex and with participation of the copper ion, accompanied by the simultaneous addition of the aryl radicals and chlorine atoms formed to the diene in the 1- and 4-positions. This leads to the formation of 1-aryl-2-chlorobut-2-enes:

$$ArN_2Cl + CuCl \rightleftarrows [ArN_2CuCl]^+Cl^- \xrightarrow{diene} [ArN_2{\cdot}diene{\cdot}Cu^-]^{2+}\ 2Cl^-;$$

$$[Ar{:}N_2{:}diene{\cdot}Cu]^{2+}2Cl^- \xrightarrow{-N_2} ArCH_2CH{-}CHCH_2Cl + CuCl;$$

diene = $CH_2{-}CH{=}CH{-}CH_2$.

The mechanism proposed also makes it possible to account for the chloroarylation of unsaturated monomers and the formation of the products of the side reactions (ArCl, telomers, additive dimers, etc.).[52]

Numerous reactions of buta-1,4-diene with ADC and other anion-substituted arenediazonium compounds have been carried out. In most cases *trans*-chloroarylbutenes are obtained in satisfactory yields (50–80%):[2,8,74,75]

$$CH_2=CH-CH=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CH=CHCH_2Cl\ ;$$

Ar=Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-$HalC_6H_4$ (where Hal=F, Cl, Br, I), 2,4-$Cl_2C_6H_3$, 2,4-$Br_2C_6H_3$, 2-, 3- and 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$, 4-$H_2NSO_2C_6H_4$, 4-$Et_2N(CH_2)_2OCOC_6H_4$,



Divinyl sulphone, in which there is virtually no conjugation between the vinyl groups, reacts with ADC to form adducts involving both one and two vinyl groups (in yields of ~50%):[76]

$$(H_2C=CH)_2SO_2 \xrightarrow[-N_2]{ArN_2Cl,CuCl_2} \begin{cases} \longrightarrow ArCH_2CHClSO_2CH=CH_2 \\ \longrightarrow (ArCH_2CHCl)_2SO_2 \end{cases};$$

Ar=Ph, 4-ClC_6H_4, 4-$O_2NC_6H_4$.

Isoprene is chloroarylated in the 1- and 4-positions with formation of 1-aryl-4-chloro-2-methylbut-2-enes (yields 65–70%):[2,75]

$$H_2C=C(Me)-CH=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2C(Me)=CHCH_2Cl\ ;$$

Ar=Ph, 4-MeC_6H_4; 4-$HalC_6H_4$ (where Hal=F, Br, I), 4-$MeOC_6H_4$, 4-$Et_2N(CH_2)_2OCOC_6H_4$.

Mono- and dichloro-substituted conjugated dienes react analogously with ADC, giving satisfactory yields of 1,4-adducts:[2,77–80]

$$H_2C=CH-CCl=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CH=CClCH_2Cl,$$

$$H_2C=CH-CH=CHCl + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CH=CHCHCl_2,$$

$$H_2C=CCl-CCl=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CCl=CClCH_2Cl\ ,$$

$$H_2C=CCl-C(Me)=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CCl=C(Me)CH_2Cl\ .$$

In its reaction with ADC piperylene combines in all cases with the Ar$^{\cdot}$ radical at the methylene group. However, the chlorine atom of the diazo-compound adds in both 2- and 4-positions of the conjugated system, forming a mixture of arylchloropentenes (overall yield 60–70%). The latter are so unstable that they lose HCl already during their isolation or purification; 1-arylpenta-1,3-dienes are obtained on a preparative scale when the above chloro-derivatives interact with bases:[81]

$$H_2C=CH-CH=CHMe + ArN_2Cl \xrightarrow[-N_2]{} \begin{cases} \longrightarrow ArCH_2CHClCH=CHMe \\ \longrightarrow ArCH_2CH=CHCHClMe \end{cases} \xrightarrow[-HCl]{} ArCH=CH-CH=CHMe\ ;$$

Ar=Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$O_2NC_6H_4$.

Bi-isopropenyl is chloroarylated to 4-chloro-2,3-dimethylbut-2-enes (in yields of 50–58%):[82]

$$H_2C=C(Me)-C(Me)=CH_2 + ArN_2Cl \xrightarrow[-N_2]{} ArCH_2C(Me)=C(Me)CH_2Cl\ ;$$

Ar=Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$MeOC_6H_4$.

The chloroarylation of conjugated dienes catalysed by $FeCl_2$ has been described. The yields of the chloroarylbutenes obtained thereby are somewhat lower (~55%); in this case the reaction is accompanied by the formation of considerable amounts of the products of the Sandmeyer reaction, telomers, and the products formed as a result of the additive dimerisation of the initial monomers.[30,31]

Tetrazonium chloride based on benzidine and diamines containing bridging R^2 groups between the benzene rings chloroarylate conjugated dienes with participation of both diazo-groups (yields 50–60%):[83–85]

$$2H_2C=CR-CH=CH_2 + \left(ClN_2-C_6H_3(R^1)-\right)_2R^2 \xrightarrow[-2N_2]{CuCl_2} \left(ClCH_2CR=CHCH_2-C_6H_3(R^1)-\right)_2R^2\ ;$$

R=H, Me, Cl; R^1=H, Me, MeO; R^2=—, S, CH_2.

Chloroarylbutenes are compounds exhibiting different types of reactivity which have been used as the starting materials for the synthesis of many new substances which are otherwise difficult to obtain. Chloroarylbutenes are readily dehydrochlorinated by bases, being converted thereby into α-arylbutadienes. In particular, a convenient method has been developed for the dehydrochlorination of chloroarylbutenes by heating in dioxan with KOH or NaOH powder, which makes it possible to obtain very satisfactory yields of α-arylbutadienes with various substituents in the benzene ring and in the side chain:[2,77]

$$ArCH_2CR=CR^1CH_2Cl \xrightarrow[-HCl]{base} ArCH=CR-CR'=CH_2\ ;$$

R=R′=H; R=Me, R′=H; R=Cl, R′=H; R=R′=Me; R=Ph, R′=H; Ar=Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$ etc.

The reactions involving the substitution of the allyl chlorine atom in chloroallylbutenes are widely used for the synthesis of 1-alkyl-4-arylbut-2-enes,[2] 1-alkoxy- and 1-amino-4-arylbut-2-enes,[79,86] the corresponding quaternary ammonium salts,[74] *N*-arylbutenyldiethanolamines,[87] *N*-arylbutenylsulphonamides,[88] and diethyl 4-arylbut-2-enylphosphonates.[89] The aldehydes $ArCH_2CH=CHCH_2CHO$, which are difficult to obtain, have been synthesised from chloroarylbutenes by the Sommelet reaction.[90] The chloroarylbutenes undergo the Vilsmeier reaction with formation of penta-2,4-dienals.[91] A novel method has been developed recently for the synthesis of diaryloctatetraenes containing substituents in the aromatic rings and in the aliphatic chain.[31]

1,4-Di(4′-chlorostyryl)- and 1,4-di(4′-nitrostyryl)-benzenes were obtained by the interaction of diazotised *p*-chloro- or *p*-nitro-aniline with 4,4′-divinylbenzene followed by the dehydrochlorination of the chloroarylation products (in yields of 14 and 30%):[71]

$$H_2C=CH-C_6H_4-CH=CH_2 + 2(4-RC_6H_4N_2Cl) \xrightarrow[-2N_2]{CuCl_2} \rightarrow 4-RC_6H_4CH_2CHCl-C_6H_4-CHClCH_2C_6H_4R\text{-}4 \rightarrow \xrightarrow[-2HCl]{KOH/C_2H_5OH} 4-RC_6H_4CH=CH-C_6H_4-CH=CHC_6H_4R\text{—}4;$$

R=Cl, NO_2.

The reaction of ADC with conjugated arylbutadienes catalysed by copper chloride is of special interest. In this case arylation takes place, namely substitution of the terminal hydrogen atom in the aliphatic chain by the aryl group of the diazo-compound. This results in the formation of conjugated 1,4-diarylbutadienes:[2,92,93]

$$4-RC_6H_4CH=CR^1-CR^2=CHR^3 + ArN_2Cl \xrightarrow[-N_2,-HCl]{CuCl_2} 4-RC_6H_4CH=CR^1-CR^2=CR^3Ar;$$

R=H, Me, Cl, NO_2; R^1=R^2=R^3=H, Me, Cl, Ar=Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$.

The interaction of α-arylbutadienes with biphenyl-4,4′-bisdiazonium chlorides entails the evolution of nitrogen from both diazo-groups. One diazo-group is involved in arylation and the other in the Sandmeyer reaction (yield ~ 35%):[94,95]

$$4-RC_6H_4CH=CR'-CH=CH_2 + ClN_2C_6H_4-C_6H_4N_2Cl \xrightarrow[-2N_2,-HCl]{CuCl_2} \rightarrow 4-RC_6H_4CH=CR'-CH=CH-C_6H_4-C_6H_4Cl\ ;$$

R=H, Me, Cl; R′=H, Me, Cl.

Apart from the reactions with ADC, the interaction of conjugated dienes with arenediazonium salts containing other anions has been described. Buta-1,4-diene reacts with benzenediazonium bromide (in the presence of $CuBr_2$ as the catalyst), giving a low yield (~20%) of $PhCH_2CH=CHCH_2Br$;[2] chloroprene is bromoarylated with satisfactory yields (50 to 58%):[96]

$$H_2C=CCl-CH=CH_2 + 3-RC_6H_4N_2Br \xrightarrow[-N_2]{} 3-RC_6H_4CH_2CCl=CHCH_2Br;$$

R=H, Me, MeO.

The interaction of buta-1,4-diene with arenediazonium sulphates and nitrates catalysed by $CuSO_4$ and $Cu(NO_3)_2$ respectively in the presence of added copper or iron powder leads to the formation of a mixture of 1,2- and 1,4-hydroxyarylbut-2-enes (in proportions of 1 : 4 and in an overall yield of ~25%). The same hydroxyarylbutenes (in proportions of 1 : 7 and in an overall yield of ~40%) are also obtained in the reaction of buta-1,4-diene with arenediazonium tetrafluoroborates in the presence of $(MeCOO)_2Cu$ as the catalyst:

$$H_2C=CH-CH=CH_2 + 4\text{-}RC_6H_4N_2X \xrightarrow[-N_2]{pH\ 5-7} \rightarrow 4\text{-}RC_6H_4CH_2CH(OH)-CH=CH_2 + 4\text{-}RC_6H_4CH_2CH=CHCH_2OH;$$
$$X = HSO_4,\ NO_3,\ BF_4;\ R = H,\ Me,\ MeO,\ NO_2.$$

The products of anion-arylation are apparently formed initially and are then hydrolysed to hydroxyarylbutenes under the reaction conditions (in an aqueous acetone medium).[97]

Buta-1,4-diene is anion-arylated by arenediazonium acetates to give 1-acetoxy-4-arylbut-2-enes (25–30%), which are smoothly converted into 1-aryl-4-hydroxybut-2-enes on alkaline hydrolysis:[98]

$$H_2C=CH-CH=CH_2 + 4\text{-}RC_6H_4N_2OCOMe \xrightarrow[-N_2]{(MeCOO)_2Cu} \rightarrow 4\text{-}RC_6H_4CH_2-CHCH_2OCOMe \xrightarrow[-MeCOOH]{H_2O} 4\text{-}RC_6H_4CH_2CH=CHCH_2OH;$$
$$R = H,\ Me,\ MeO.$$

Buta-1,4-diene and isoprene react with arenediazonium tetrafluoroborates in aqueous alcoholic media to form 1-alkoxy-4-arylbut-2-enes (in yields of 30–50% for primary alcohols); secondary alcohols give low yields (~15%), while tertiary alcohols hardly react:[99]

$$H_2C=CR-CH=CH_2 + 4\text{-}R'C_6H_4N_2BF_4 \xrightarrow[-N_2,\ -HF,\ -BF_3]{AlkOH,\ (MeCOO)_2Cu} \rightarrow 4\text{-}RC_6H_4CH_2R'C=CHCH_2OAlk,$$
$$R = H,\ Me;\ R' = H,\ Me,\ Cl;\ Alk = Me,\ Et,\ Pr,\ iso\text{-}Pr,\ Bu,\ PhCH_2.$$

In the presence of ethylene glycol the above dienes are alkoxylated with participation of both hydroxyls and give 35–57% yields of the ethers $(4\text{-}R'C_6H_4CH_2CR=CHCH_2OCH_2)_2$.[99]

On interaction with arenediazonium sulphates, nitrates, and tetrafluoroborates in the presence of sodium nitrate, sodium halides, or sodium salts of carboxylic acids and with catalysis by $(MeCOO)_2Cu$, the same dienes combine with the aryl groups of the diazo-compounds and the anions of the corresponding sodium salts at the ends of the conjugated system to form anion-arylation products (25–45%):[100]

$$H_2C=CR-CH=CH_2 + ArN_2X \xrightarrow[-N_2,\ -NaX]{NaHal} ArCH_2CR=CHCH_2Hal;$$
$$R = H,\ Me;\ X = SO_4H,\ NO_2,\ BF_4;$$
$$Hal = NO_2,\ F,\ Cl,\ Br,\ MeCOO,\ EtCOO,\ PrCOO;$$
$$Ar = Ph,\ 4\text{-}MeC_6H_4,\ 4\text{-}ClC_6H_4.$$

On interaction with arenediazonium tetrafluoroborates or sulphates in the presence of potassium salts of *O,O*-dialkyl or *O,O*-diphenyl phosphorodithioates, buta-1,4-diene and isoprene give rise to 1,4-adducts (in 66–80% yields):[101]

$$H_2C=CR-CH=CH_2 + 4\text{-}R^1C_6H_4N_2X \xrightarrow[-N_2,\ -KX]{(R^2O)_2P(S)SK,\ CuCO_3(OH)_2} \rightarrow 4\text{-}R^1C_6H_4CH_2CR=CHCH_2SP(S)(OR^2)_2;$$
$$R = H,\ Me;\ X = BF_4,\ HSO_4;\ R^2 = Me,\ Et,\ Pr,\ iso\text{-}Pr,\ Bu,\ iso\text{-}Bu,\ Ph.$$

5. Vinyl Ethers and αβ-Unsaturated Aldehydes and Ketones

Vinyl acetate results with ADC[102] (and also with arenediazonium tetrafluoroborates[103]) to form 1-acetoxy-2-aryl-1-chloroethanes (in yields of 30–50%), which readily hydrolyse on steam distillation, giving high yields (~90%) of arylacetaldehydes:[104]

$$MeCOOCH=CH_2 + ArN_2X \xrightarrow[-N_2]{CuCl_2} MeCOOCHClCH_2Ar \xrightarrow[-HCl,\ -MeCOOH]{H_2O} ArCH_2CHO;$$
$$Ar = Ph,\ 4\text{-}MeC_6H_4,\ 4\text{-}MeOC_6H_4,$$
$$2\text{-}\text{ и }4\text{-}ClC_6H_4,\ 4\text{-}BrC_6H_4;\ X = Cl,\ BF_4.$$

A method of synthesis of α-arylketones by the reaction of ADC with enol acetates has been proposed. For this purpose, enol acetate (or enol benzoate or disulphide) is obtained from the initial ketone. On interaction with ADC, the acetate is arylated in the α-position in the ethylene group. After the removal of the acetyl group (by hydrolysis), the α-arylketone is obtained. $ArCH_2COMe$ (from acetone), $ArCH_2COPh$ (from acetophenone), ArPhCHCOPh (from benzyl phenyl ketone), etc. have been obtained in this way:[103,105]

$$RCOMe \xrightarrow[-AcOH]{Ac_2O} RC(OAc)=CH_2 \xrightarrow[-N_2,\ -HCl]{ArN_2Cl,\ CuCl} RC(OAc)=CHAr \xrightarrow[-AcOH]{H_2O+} RCOCH_2Ar,$$
$$R = Me,\ PhCH_2;\ Ar = 4\text{-}ClC_6H_4.$$

Acrolein and crotonaldehyde are chloro- and bromophenylated, combining with the halogen and the $Ph^{\cdot}$ radical at the ethylenic bond in the α- and β-positions respectively. Best results (yields of 20–50%) are achieved when the reaction is carried out at 0–2 °C and pH ~ 7 (Dombrovskii[2]):

$$RHC=CHCHO + PhN_2X \xrightarrow[-N_2]{CuX_2} RCH(Ph)CHXCHO;$$
$$R = H,\ Me;\ X = Cl,\ Br.$$

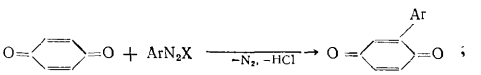
Methyl vinyl ketone is chloroarylated analogously, forming α-chloro-substituted aliphatic-aromatic ketones (yields 20 to 40%):[2]

$$MeCOCH=CH_2 + RC_6H_4N_2Cl \xrightarrow[-N_2]{CuCl_2} MeCOCHClCH_2C_6H_4R;$$
$$R = 4\text{-}Cl,\ 4\text{-}O_2N,\ 4\text{-}COOH.$$

Aryl vinyl and aryl isopropenyl ketones react in the same way, forming unstable aryl β-aryl-α-chloroethyl ketones (yields 25–40%); some of these are dehydrochlorinated even on vacuum distillation and are converted into chalcones:[106]

$$Ar'COCR=CH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} Ar'COCRClCH_2Ar \xrightarrow{-HCl} Ar'COCR=CHAr;$$
$$R = H,\ Me;\ Ar = Ph,\ 4\text{-}O_2NC_6H_4;$$
$$Ar' = Ph,\ 4\text{-}MeC_6H_4,\ 2,4\text{-}Me_2C_6H_3,$$
$$4\text{-}Cl\text{- and }4\text{-}BrC_6H_4$$

Quinones undergo a vigorous arylation reaction with arenediazonium salts, a distinctive feature of which is that it proceeds in the absence of catalysts owing to the low redox potential of the quinonoid system.[31] The arylation of *p*-benzoquinone has been widely investigated. This reaction constitutes an excellent method of synthesis of numerous monoaryl-*p*-benzoquinones, whose yields frequently reach 80–90%:[2,6]

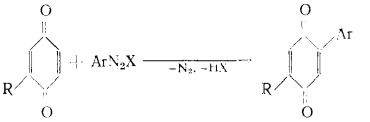


$$+ ArN_2X \xrightarrow[-N_2,\ -HCl]{}$$

;

Ar = Ph, 2- and 4-MeC_6H_4, 2-, 3- and 4-ClC_6H_4, 2,6-$Cl_2C_6H_3$, 2-BrC_6H_4, 2,6-Me_2-4-BrC_6H_2, 4-HOC_6H_4, 2- and 4-$MeOC_6H_4$, 2,4-$(MeO)_2C_6H_3$, 2-, 3- and 4-$O_2NC_6H_4$, 4-$MeCOC_6H_4$, 4-$HOCOC_6H_4$, 3-$MeOCOC_6H_4$, 2-PhC_6H_4, 4-PhC_6H_4, 4-$H_2NSO_2C_6H_4$, 1- and 2-$C_{10}H_7$; $X = HSO_4^-,\ Cl^-,\ Br^-,\ PO_4^{3-}$.

Monosubstituted *p*-benzoquinones are arylated predominantly in the 5-position for steric reasons, forming 2-R-5 aryl-*p*-benzoquinones in satisfactory yields:[2,6]



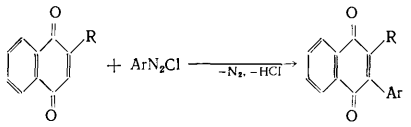
$$+ ArN_2X \xrightarrow[-N_2,\ -HX]{}$$

;

R = Me, Cl, Ph, 4-ClC_6H_4, 2-$O_2NC_6H_4$, 4-$MeOCOC_6H_4$; Ar = Ph, 3- and 4-ClC_6H_4, 2- and 3-BrC_6H_4, 2,- 3- and 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$, 4-$MeOCOC_6H_4$, 1- and 2-$C_{10}H_7$; X = HSO_4, Cl.

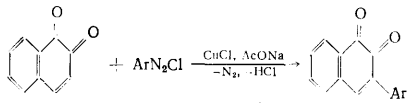
2,3-, 2,5-, and 2,6-Disubstituted *p*-benzoquinones are effectively arylated by diazo-compounds (the 2,3-derivatives in the 5-position and the 2,5- and 2,6-derivatives in the 3-position).[2,6]

1,4-Naphthoquinone and its 2-substituted derivatives are arylated to 2-aryl-1,4-naphthoquinones and 2-R-3-aryl-1,4-naphthoquinones respectively (in moderate yields):[2,6]



R=H, Me, OH, MeO; Ar=Ph, 2- and 4-MeC_6H_4, 4-ClC_6H_4, 4-$MeOC_6H_4$, 3- and 4-$O_2NC_6H_4$, 4-HOC_6H_4, 4-$HOSO_2C_6H_4$, 3-HO-4-$HOCOC_6H_4$, 2-$C_{10}H_7$.

1,2-Naphthoquinone is arylated in the presence of the CuCl catalyst in acetate buffer, giving low yields (5–37%) of 3-aryl-1,2-naphthoquinones:[107]



Ar = 2-, 3- and 4-ClC_6H_4.

6. αβ-Unsaturated Acids and Their Derivatives

The reactions of αβ-unsaturated carboxylic acids their derivatives with ADC have been investigated and described fairly completely. A survey of the available data shows that the reactions of αβ-unsaturated carboxylic acids in which the carboxyl is conjugated with electron-accepting groups proceed with substitution of the vinyl α-hydrogen atom by the Ar· radical derived from the diazo-compound with simultaneous decarboxylation and elimination of HCl.

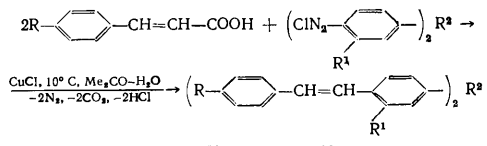
Thus the reactions of β-arylacrylic (cinnamic) acids with ADC proceed via this pathway and constitute the basis of a convenient and simple method of synthesis of numerous stilbenes, whose yields are in most cases good or entirely satisfactory:[2,6]

$$RCX{=}CHCOOH + ArN_2Cl \xrightarrow[-N_2,\,-CO_2,\,-HCl]{CuCl_2 \text{ or } CuCl} RCX{=}CHAr;$$

X = H, Ph, or other aryl groups;
Ar = Ph or other aryl groups.

Fluorine-containing stilbenes 4-$HOC_6H_4CH{=}CHC_6H_4CF_3$ and 4-$EtOCOC_6H_4CH{=}CHC_6H_4CF_3$-4 have been obtained in this way from diazotised fluoroanilines and cinnamic acid derivatives (yields of 60 and 33%).[108]

On interaction with tetrazonium chlorides, i.e. the chlorides of diphenylbisdiazonium, 3,3'-dinitrobiphenylbisdiazonium, methylenebis(benzenediazonium), oxybis(benzenediazonium), and bis(diazoniaphenyl) sulphone, cinnamic acid give rise to the corresponding bis-stilbenes (in ~50% yield), which exhibit a semiconductor type sensitivity to light:[109]



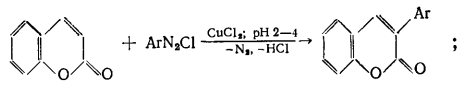
R=H, MeO, NO_2, Me_2N;
R^1=H, NO_2; R^2=—, O, SO_2, CH_2

β-Aroylacrylic acids react analogously with ADC, forming as a rule chalcones in high yields, which constitutes an effective method of synthesis of these compounds:[2,6,110]

$$RCOCH{=}CHCOOH + ArN_2Cl \xrightarrow[-N_2,\,-CO_2,\,-HCl]{CuCl_2} RCOCH{=}CHAr;$$

R = Ph or other aromatic groups;
Ar=2-, 3- and 4-$HalC_6H_4$ (where Hal=Cl, Br), or 2- 3- and 4-$O_2NC_6H_4$

Coumarin and unbelliferone are arylated in the α-position relative to the carbonyl group, forming 3-arylcoumarins (in yields up to 80%):[2,6,42]



Ar=4-ClC_6H_4, 2-, 3- and 4-$O_2NC_6H_4$ etc.

In the reactions of ADC with maleic acid one of the COOH groups is split off and cinnamic acids are obtained as a result (in yields of ~60%):

$$\begin{matrix} HC{-}COOH \\ \| \\ HC{-}COOH \end{matrix} + ArN_2Cl \xrightarrow[-N_2,\,-CO_2,\,-HCl]{CuCl_2} ArCH{=}CHCOOH;$$

Ar=2-, 3- and 4-ClC_6H_4, 2.6-$Cl_2C_6H_3$ etc.

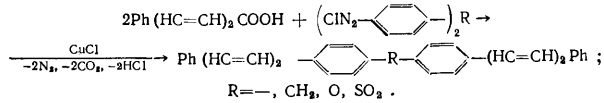
In the arylation of citraconic or bromomaleic acid the COOH group adjoining the methyl group or the bromine atom respectively is split off.[2,6]

Under the conditions of the Meerwein reaction, sorbic and cinnamylideneacetic acids are arylated at the α-carbon atom with simultaneous decarboxylation. This results in the formation of 4-aryl-1-methyl- and 1,4-diaryl-buta-1,3-dienes (for the latter, this reaction is one of the effective methods of synthesis):[2,6]

$$R(CH{=}CH)_2COOH + ArN_2Cl \xrightarrow[-N_2,\,-CO_2,\,-HCl]{CuCl_2} R(CH{=}CH)_2Ar;$$

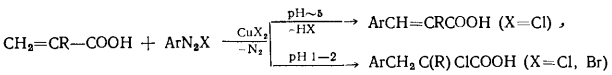
R=Me, Ph; Ar=2-, 3- and 4-ClC_6H_4, 2- and 4-$MeOC_6H_4$, 3- and 4-PhC_6H_4.

Cinnamylideneacetic acid reacts also with aromatic tetrazonium chlorides forming bisbutadienes (in yields up to 64%):[109]



R=—, CH_2, O, SO_2.

In media close to neutrality acrylic and crotonic acids are arylated at the β-carbon atom with retention of the carboxy-group, while in acid media they are halogenoarylated also with retention of the carboxy-group:[2,111]



R=H, Me; Ar=2- and 4-MeC_6H_4, 2-, 3- and 4-ClC_6H_4, 2-, 3- and 4-BrC_6H_4, 2-, 3- and 4-$O_2NC_6H_4$, 2- and 4-$MeOC_6H_4$, 1-$C_{10}H_7$.

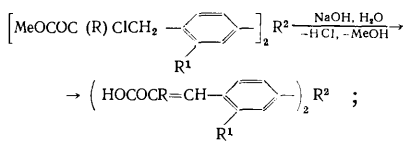
Methyl acrylate and methacrylate react with ADC, combining with a chlorine atom in the α-position and with the aryl radical derived from the diazo-compound in the β-position. This results in the formation of chloroarylation products (the yields reach 70%).[2,112,113] The products obtained from acrylic acid and its derivatives are valuable starting materials for the synthesis of substituted cinnamic acids and their esters and, after aminolysis, they serve as a source of phenylalanines with various substituents in the benzene ring:[2,6]

$$H_2C{=}CRCOOMe + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2C(R)ClCOOMe \xrightarrow[H_2O]{NH_3} \rightarrow ArCH_2CR(NH_2)COOH;$$

R=H, Me, Cl, Br; Ar=Ph etc.

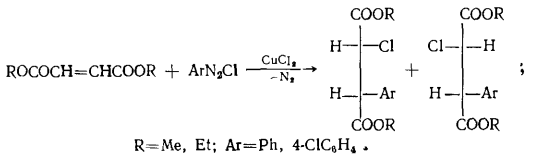
The reactions of methyl acrylate and methacrylate with bisdiazotised 4,4'-diaminobiphenyls, di(4-aminophenyl)-methane, and di(4-aminophenyl) ether proceed via two

pathways: chloroarylation with participation of both diazo-groups (the main reaction with yields of products of 42–62%) and chloroarylation with participation of only one diazo-group and the replacement of the second diazo-group by a chlorine atom via the Sandmeyer reaction (yields 5–21%). The reactions are catalysed by both $CuCl_2$ and $FeCl_2$, but the latter promotes the formation of telomers. The bischloro-arylation products are smoothly dehydrochlorinated and hydrolysed by alkali, being converted into the corresponding biscinnamic acids:[114]



R=H, Me; R^1=H, MeO, NO_2; R^2=O, CH_2.

The reactions of maleate and fumarate esters with ADC proceed mainly as *trans*-addition of the Ar$^{\cdot}$ radical and a chlorine atom to the ethylenic bonds in fumarate esters, to which the maleate esters also isomerise under the reaction conditions.[115] This results in the formation of a mixture of the *erythro*- and *threo*-forms in proportions of 72 : 28:[115,116]



R=Me, Et; Ar=Ph, 4-ClC_6H_4.

Acrylamide undergoes the chloroarylation reaction and gives satisfactory yields (60–70%) of β-aryl-α-chloropropion-amides, whose dehydrochlorination by organic bases results in their smooth conversion into β-arylacrylamides, which is also of synthetic interest:[117]

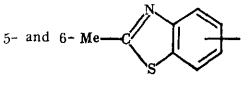
$$H_2C{=}CHCONH_2 + ArN_2Cl \xrightarrow[-N_2]{CuCl_2} ArCH_2CHClCONH_2 \xrightarrow[-HCl]{Et_3N} ArHC{=}CHCONH_2;$$

Ar=Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-, 3- and 4-$O_2NC_6H_4$.

Acrylonitrile, the most important derivative of an αβ-unsaturated acid, is widely used in reactions with numerous ADC, which results in good yields (up to 90%) of β-aryl-α-chloropropionitriles. The reactions are catalysed by $CuCl_2$, CuCl, and other catalysts:[2,6,18,19,118,119]

$$H_2C{=}CHCN + ArN_2Cl \xrightarrow[-N_2]{} ArCH_2CHClCN;$$

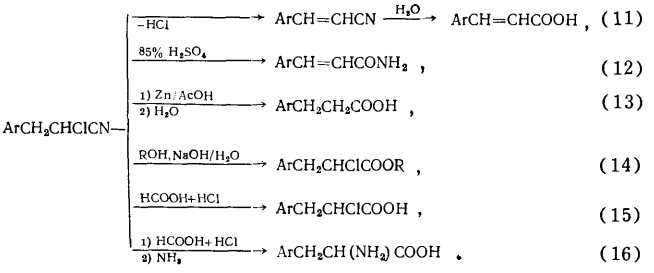
Ar=Ph, 2-, 3- and 4-MeC_6H_4, 2-, 3- and 4-ClC_6H_4, 2.4-$Cl_2C_6H_3$, 2-, 3- and 4-BrC_6H_4, 2-, 3- and 4-$O_2NC_6H_4$, 2.4-$(O_2N)_2C_6H_3$, 4-$MeOC_6H_4$, 4-NCC_6H_4, 4-$HOSO_2C_6H_4$, 1- and 2-$C_{10}H_7$,



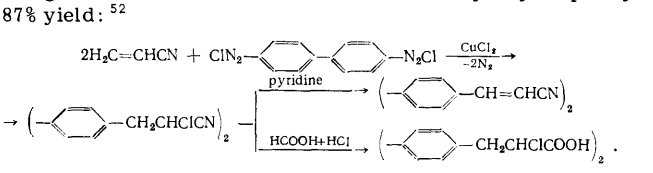
α-Methyl- and α-chloro-acrylonitriles form analogously β-aryl-α-chloroisobutyronitriles $ArCH_2C(Me)ClCN$ [120] and β-aryl-αα-dichloroacrylonitriles $ArCH_2CCl_2CN$ [121] respectively in yields of 50–70%:

(Ar=Ph, 4-MeC_6H_4, 4-Cl and 4-BrC_6H_4, 4-$MeOC_6H_4$, 2-, 3- and 4-$O_2NC_6H_4$).

Arylchloropropionitriles have served as starting materials for the synthesis of new compounds which are otherwise difficult to obtain. Thus they are readily dehydrochlorinated by bases, being converted almost quantitatively into the nitriles of cinnamic acids, whose hydrolysis give rise to the corresponding acids [reaction (11)],[2,118,119] or their amides [reaction (12)].[122] The successive reduction and hydrolysis of chloropropionitriles make it possible to obtain hydro-cinnamic acids [reaction (13)],[2] while alkaline hydrolysis in aqueous alcohol gives rise to esters of α-chlorohydrocinnamic acids [R = Me or Et; reaction (14)].[2] It has been suggested that the ester 4-$ClC_6H_4CH_2CHClCOOMe$ be used to eradicate wild oats in wheat fields.[123,124] The hydrolysis of chloro-propionitriles with a mixture of concentrated formic and hydrochloric acids gives rise to β-aryl-α-chloropropionic acids in ~95% yields [reaction (15)];[2] hydrolysis with the same mixture of acids followed by treatment with ammonia or urotropine results in the formation of D,L-arylalanines and their derivatives from arylchloropropionitriles [reaction (16)]:[2,125]

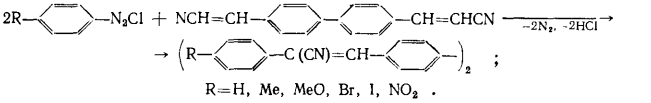


Biphenyl-4,4′-bisdiazonium chloride reacts with acrylo-nitrile with evolution of nitrogen from both diazo-groups and produces 4,4′-bis(2-chloro-2-cyanoethyl)biphenyl in 78% yield. The latter is readily dehydrochlorinated and con-verted into 4,4′-bis(2-cyanoethylene)biphenyl in 71% yield and on heating with a mixture of concentrated HCOOH and HCl it gives rise to 4,4′-bis(2-chloro-2-carboxyethyl)biphenyl in 87% yield:[52]



Acrylonitrile gives rise analogously to the chloroarylation products $X(C_6H_4CH_2CHClCN)_2$, where X = CH_2 or S, on reaction with methylenebis(benzenediazonium) and thiobis-(benzenediazonium)chlorides (yields 44 and 66% respec-tively).[52]

In reactions with ADC, 4,4′-bis(2-cyanovinyl)biphenyl is arylated in the α-position relative to the CN group (reactant ratio 1 : 2, catalyst CuCl, pH 2–4, aqueous acetone medium), giving rise to bisarylation products–4,4′-di(cyanostyryl)-biphenyls (yields 33–52%):[126]



R=H, Me, MeO, Br, I, NO_2.

The anion-arylation of acrylonitrile by the diazonium salts $ArN_2^+A^-$ also proceeds with addition of the anion A^- and the radical derived from the diazo-compound in the α- and β-positions of the ethylenic bond respectively. It has been shown that the interaction of acrylonitrile with arenediazonium sulphates in the presence of thiocyanate ions and catalytic amounts of copper(I) thiocyanate leads to β-aryl-α-thio-cyanatopropionitriles (in yields of ~60%).[47] In this case considerable amounts of ArSCN (up to 35%) are also obtained.[127] Arenediazonium thiocyanates are apparently

formed initially in the exchange reaction and then react further with acrylonitrile in accordance with a familiar mechanism:

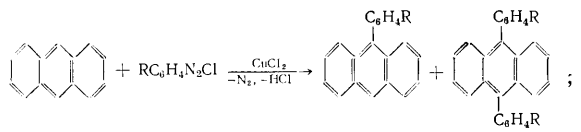
$$ArN_2HSO_4 + NH_4SCN \rightleftarrows ArN_2SCN + NH_4HSO_4,$$
$$H_2C{=}CHCN + ArN_2SCN \xrightarrow[-N_2]{CuSCN} ArCH_2CH(SCN)CN;$$
Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2-$O_2NC_6H_4$.

β-Aryl-α-(*O*-ethyl dithiocarbonato)propionitriles have been obtained analogously in the presence of potassium and copper(I) ethylxanthates,[128] while in the presence of sodium and copper(I) diethyl phosphorodithioates the products are β-aryl-α-(*O*,*O*-diethyl phosphorodithioato)propionitriles (in yields of 40–72%):[129]

$$H_2C{=}CHCN + 4\text{-}RC_6H_4N_2HSO_4 \xrightarrow{-N_2}$$
$$\rightarrow \begin{cases} \xrightarrow[EtOC(S)SCu]{EtOC(S)SK} 4\text{-}RC_6H_4CH_2CH[SC(S)OEt]CN, & (a) \\ \xrightarrow[(EtO)_2P(S)SCu]{(EtO)_2P(S)SNa} 4\text{-}RC_6H_4CH_2CH[SP(S)(EtO)_2]CN; & (b) \end{cases}$$
(a) R = H, NO_2; (b) R = NO_2.

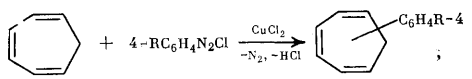
7. Aromatic Systems

In conclusion we shall consider data on the arylation of aromatic systems under the conditions of the Meerwein reaction or similar conditions. Benzene, toluene, xylenes, halogenobenzenes, and nitrobenzenes are apparently hardly arylated under the conditions of this reaction. However, certain polycyclic aromatic systems enter into the arylation reaction. Thus anthracene is arylated by ADC, forming mixtures of 9-aryl- and 9,10-diarylanthracenes, whose yields vary from 7 to 54%:[130]



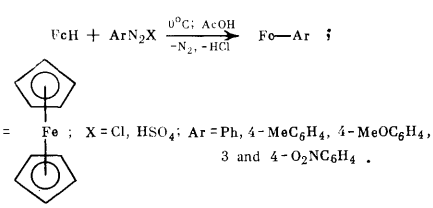
R = H, 4-Cl, 4-MeO, 2-NO_2, 4-NO_2.

Cyclohepta-1,3,5-triene is also arylated, giving low yields (7–29%) of arylcycloheptatrienes (the position of the Ar group has not been established):[131]

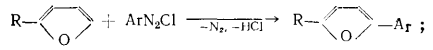


R = H, Cl, NO_2.

It has been shown in the studies of Nesmeyanov, Perevalova, and co-workers[132–134] that ferrocene is arylated by arenediazonium salts in the absence of catalysts, giving satisfactory yields (~60%) of arylferrocenes:



Among heteroaromatic compounds, substituted furans proved to be the most reactive in relation to ADC. Furan itself is arylated in the α-position with low yields.[135,136] α-Substituted furans, namely furfural, 2-acetylfuran, furan-2-carboxylic acid, and furyl-2-nitroethylene, are arylated in the 5-position on interaction with various ADC (in the presence of $CuCl_2$ or CuCl as the catalysts), giving rise to 5-aryl-2-substituted furans, whose yields vary from 6 to 80%:



R = CHO, Ar = 3-$O_2NC_6H_4$, 4-HOC_6H_4, 4-PhC_6H_4, 4-(4-$MeOC_6H_4$)C_6H_4 137—139; R = COMe, Ar = 4-ClC_6H_4, 4-BrC_6H_4, 4-$O_2NC_6H_4$ 140; R = COOH, Ar = 3- and 4-ClC_6H_4, 4-BrC_6H_4, 3- and 4-$O_2NC_6H_4$ 141, 142; R = COOAlk (Alk = Me, Et, Pr), Ar-2-, 3- and 4-ClC_6H_4, 2- and 3-$O_2NC_6H_4$, 2,4-$(O_2N)_2C_6H_3$ 136, 142; R = COCOOH, Ar = 4-BrC_6H_4 143; R = CH=$CHNO_2$, Ar = 4-ClC_6H_4, 4-BrC_6H_4, 4-$O_2NC_6H_4$ 144.

The data described show that the scope of the reactions of unsaturated compounds with aromatic diazo-compounds has not been exhausted. There is apparently no doubt about the radical mechanism of the reactions catalysed by transition metal salts and in the first place by copper chlorides. There is a need for further studies in order to elucidate the details of the mechanism of the conversion of the olefin–catalyst–aromatic diazo-compound complex, which results in the formation of anion-arylation and arylation products. The latter is apparently a process involving the addition-elimination of the elements of arenediazonium at the multiple bond of the unsaturated compound.

Further expansion of the range of unsaturated compounds and aromatic diazo-compounds used in the Meerwein reaction in order to obtain aliphatic-aromatic compounds containing several reaction centres is of undoubted interest for organic synthesis. The improvement of the anion-arylation and arylation methods will make it possible to reduce to a minimum the competing reactions, which will reduce the amount of side products.

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Nezhinsk Pedagogic Institute

Translated from *Uspekhi Khimii*, 53, 1648-1674 (1984) U.D.C. 547.85 + 547.86

The Reactions of Azines on Treatment with 1,3-Bifunctional Nucleophiles

V.N.Charushin and O.N.Chupakhin

The literature data on the *o*-cyclisation reactions of azines with 1,3-bifunctional nucleophiles, which make it possible to annelate furan, pyrrole, imidazole, and other five-membered rings to an aromatic aza-ring are surveyed and described systematically. The cyclisation reactions leading to *m*-linked cyclic adducts or products of the transformation of azines via the intermediate formation of cyclic *m*- and *p*-adducts are also examined.
The bibliography includes 152 references.

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I. INTRODUCTION

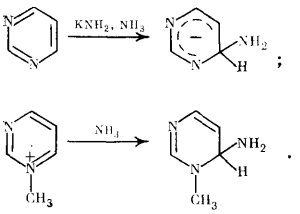
The reactions of azines with simple nucleophiles have been considered in fair detail in a whole series of books, monographs, and reviews.[1-12] Rules have been established for the nucleophilic substitution in the series of azines which make it possible to predict the rates of these reactions as a function of the number of aza-groups and their positions in the ring, the influence of other substituents, benzoannelation, the nature of the leaving group, and other factors.[1-3, 10,11] The characteristics of the nucleophilic substitution of hydrogen[7-9] as well as the wide variety of transformdtions of azines and azinium salts under the influence of ammonia, potassium amide, hydrazine, and other simple nucleophiles have been investigated.[4-6]

An increasing number of communications concerning the reactions of azines with 1,3-bifunctional nucleophiles have been published in recent years; as a rule, these reactions are more complex, more varied, and sometimes also unexpected, The present review is devoted to the rules governing these reactions and their characteristic features. Before discussing the reactions of azines with 1,3-dinucleophiles, we shall consider briefly certain reactions of azines with simple nucleophiles.

II. CHARACTERISTIC FEATURES OF REACTIONS OF AZINES WITH SIMPLE NUCLEOPHILES

1. σ-Adducts of Azines

It is nowadays considered as generally recognised that the first stage in many reactions of azines with nucleophiles is the formation of σ-adducts. The σ-adducts are understood to be both anionic σ-complexes of azines, which are close analogues of Meisenheimer complexes, and uncharged dihydrocompounds, which are formed as a result of the addition of neutral nucleophiles to an uncharged aromatic aza-ring or in reactions of azinium cations with anionic and neutral reagents.[13-42]. The anionic σ-complex of pyrimidine with potassium amide[33] and the neutral amino-adduct formed on dissolving an *N*-methylpyrimidinium salt in liquid ammonia[31] can serve as examples.



The development and application of the ^1H and ^{13}C NMR spectroscopic methods made it possible to accumulate during the last 10–15 years extensive factual data on the direct detection of anionic σ-complexes and neutral σ-adducts for the majority of azines (pyridine,[18-20] quinoline and isoquinoline,[18,21,22] acridine,[23,24] pyrimidine,[17,25-32] other diazines and benzodiazines,[17,18,33-36] triazines,[15,16] pteridine,[37-39] naphthyridines,[40,41] *s*-tetrazine,[42] as well as a series of aromatic polynitro-compounds related to the above substances in terms of a series of chemical properties[43-46]). For example, the series of *N*-adducts attained in the reactions of azines with liquid ammonia or with potassium amide in liquid ammonia is fairly varied and representative (Table 1). The *O*-adducts formed in the reactions involving the covalent hydration of *N*-alkylazinium cations[13] and the products of the *C*-addition of the cyanide anion to acylazinium salts (Reissert's compounds)[14] have also been fairly thoroughly investigated.

The data presented in Table 1 make it possible to compare the spectroscopic characteristics of the anionic and neutral amino-adducts of azines and also to trace their variation as a function of the position of the aza-group relative to the sp^3-carbon atom. A characteristic feature of the ^1H NMR spectra of both anionic and neutral σ-adducts is the signal in the range 3.7–5.5 p.p.m. (Table 1), i.e. the signal displaced upfield by 3.5–5.0 p.p.m. compared with the signals of the initial substrates, which has been assigned to the proton at the tetragonal carbon atom. In the anionic σ-complexes of pyridine, quinoline, and isoquinoline the proton at the sp^3-carbon atom (H_α) absorbs in weaker fields, while that at the neighbouring carbon atom ($H\beta$) absorbs in stronger fields compared with the corresponding signals of the uncharged *N*-methyl analogues (Table 1). It is also seen from the examples presented that the constants for the spin–spin interaction (CSSI) between the corresponding protons of the

heterocycle are reduced by ~1 Hz on passing from neutral σ-adducts to the anionic adducts, but overall their ^{1}H NMR spectra are extremely similar.

Table 1. ^{1}H NMR spectra of the anionic and neutral σ-adducts of azines in liquid ammonia.

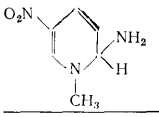
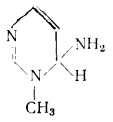
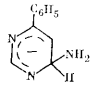
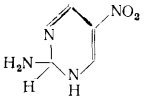
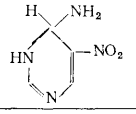
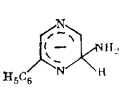
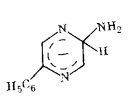
Adduct	δ, p.p.m.		CSSI, Hz	References
	proton at tetragonal carbon atom	protons of heterocycle		
	H(6):5.06	H(2):8.49; H(4):6.85; H(5):5.38	$J_{4,5}=10$; $J_{5,6}=4$	[18]
	H(6):4.57	H(2):6.94; H(4):6.27; H(5):4.91	$J_{4,5}=7$; $J_{5,6}=4.5$	[31]
	H(4):4.63	H(2):7.07; H(5):4.32	$J_{2,4}=J_{2,6}=0.5$; $J_{2,5}=1.5$; $J_{4,5}=3.5$; $J_{5,6}=6.5$	[33]
	H(2):4.26	H(5):5.43; H(6)*	$J_{5,6}=4.5$	[26]
	H(6):4.71	H(2):7.20; H(5):4.92	$J_{5,3}=4.0$	[26]
	H(2):5.33	H(4,6):8.18	$J_{2,4}=J_{2,6}=1.3$	[32]
	H(4):5.45	H(2):7.57; H(2):8.22	—	[32]
	H(4):3.73	H(3):6.55; H(5):4.27; H(6):6.70	$J_{3,4}=3.5$; $J_{3,5}=3.0$; $J_{3,6}=0.5$; $J_{4,5}=4.5$; $J_{5,6}=7.0$	[33]
	H(2):4.22	H(3):5.61; H(5):5.82; H(6):6.60	$J_{2,3}=3.0$; $J_{3,6}=0.5$; $J_{5,6}=3.0$	[33]
	H(6):4.33	H(3)*; H(5):5.70	$J_{5,6}=2.5$	[17]
	H(5):4.16	H(3)*; H(6):5.93	$J_{5,6}=2.5$	[17]

Table 1 (contd.).

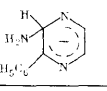
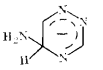
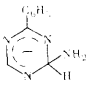
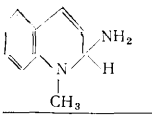
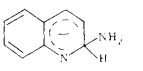
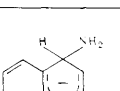
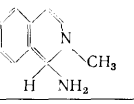
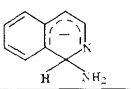
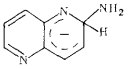
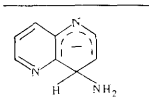
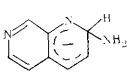
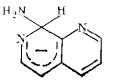
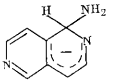
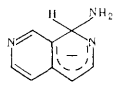
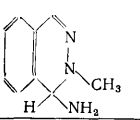
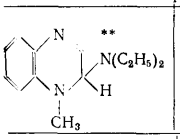
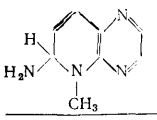
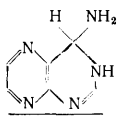
Adduct	δ, p.p.m.		CSSI, Hz	References
	proton at tetragonal carbon atom	protons of heterocycle		
	H(3):5.35	H(5):6.76; H(6):6.03	$J_{5,6}=2.5$	[17]
	H(5):4.15	H(3):7.40; H(6):6.65	—	[16]
	H(2):5.33	H(6):7.31	—	[15]
	H(2):4.79	H(3):5.86; H(4)*	$J_{2,3}=5.5$; $J_{3,4}=9.8$	[18]
	H(2):5.10	H(3):5.20; H(4)*	$J_{2,3}=4.3$; $J_{3,4}=9.0$	[21]
	H(4):4.70	H(2)* H(3):4.20	$J_{2,3}=6.5$; $J_{3,4}=4.3$	[21]
	H(1):5.15	H(3):6.37; H(4):5.45	$J_{1,3}=1.2$; $J_{3,4}=7.0$	[18]
	H(1):5.32	H(3)* H(4):4.87	$J_{3,4}=5.5$	[21]
	H(2):4.97	H(3):5.38; H(4)*	—	[40]
	H(4):4.59	H(2)*; H(3):4.18	—	[40]
	H(2):5.02	H(3):5.31; H(4):6.28	—	[40]
	H(8):5.13	H(5):4.52; H(6):7.01	—	[40]
	H(1):5.03	H(3):7.09; H(4):4.70	—	[41]
	H(1):5.03	H(3):7.16; H(4):4.59	—	[41]
	H(1):5.13	H(4):7.55	—	[18]

Table 1 (contd.).

Adduct	δ, p.p.m.		CSSI, Hz	References
	proton at tetragonal carbon atom	protons of heterocycle		
	H(2):4.70***	H(3):7.41	$J_{2,3} = 3.5$	[36]
	H(6):5.18	H(7):6.40; H(8):6.73	$J_{6,7} = 4.5$; $J_{7,8} = 10$	[18]
	H(4):5.52	H(2):7.64	—	[37]

*The signal of this proton is overlapped by the multiplet due to the aromatic protons in the range 7.0–7.7 e.p.m.
**The adduct with ammonia has not been described.
***In deuterochloroform.

The formation of σ-adducts as the primary σ-linked products of the interaction is characteristic of various types of reactions of azines with simple nucleophiles: nucleophilic substitution of hydrogen,[7,8,23,24,32,40] substitutions via the $S_N(ANRORC)$† mechanism,[6] reactions leading to transformations of the heterocyclic systems,[4,5] and other reactions.

2. The Polydentate Nature of Azines

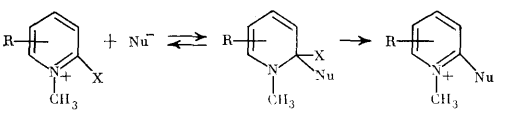
The outcome of the reactions of azines with nucleophiles and in general with 1,3-dinucleophiles in particular is in many respects determined by the properties of the σ-adducts, their stability, and the subsequent reactions which they undergo. The situation is complicated by the fact that many azines are polydentate and form two or even several types of σ-adducts with simple nucleophiles with respect to different positions in the heterocycle (Table 1). On the basis of the chemical shifts of the protons and the values of the CSSI in the ^{1}H NMR spectra of the σ-adducts, it is possible to determine accurately the reaction centre, i.e. the carbon atom which forms a covalent bond with the nucleophile. Since the values of CSSI characteristic of addition to a particular position in the azine ring change insignificantly as the substituent at the sp^3-carbon atom is varied, the data in Table 1 for the amino-adducts can be used to analyse the composition of the reaction mixtures of azines with other nucleophiles.

In cases of competitive addition of a nucleophile to two positions in the heterocycle an important factor is how the reaction is controlled under the given conditions—kinetically or thermodynamically. As a rule, the *o*-position relative to the heteroatom, i.e. the C(2) carbon atom, is more vulnerable to nucleophilic attack, while under the conditions of thermodynamic control more stable σ-adducts involving the C(4) position are formed. The formation of C(2)- and C(4)-linked σ-adducts in the reactions of pyridinium[19,20] and quinolinium[22] salts with *C*-nucleophiles as well as the formation of 2- and 4-amino-adducts of 1,5-naphthyridine[40] and 5-nitropyrimidine[32] in reactions with liquid ammonia (Table 1) may be quoted as examples of compounds obtained in recent years.

†Addition of the nucleophile, ring opening, and ring closure.

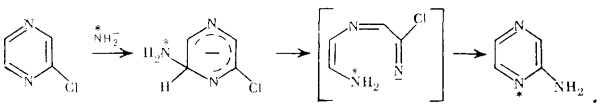
3. Chemical Reactions of the σ-Adducts

The stability of the σ-adducts depends both on the conditions of their formation and on the structure of the azines and varies within wide limits. The pathways whereby they can be stabilised are also varied. One of these pathways is the aromatisation of the σ-adducts as a result of the elimination of the substituent X, which represents overall aromatic nucleophilic substitution (S_NAE):



If X is a group which can be readily eliminated, then aromatisation usually proceeds so rapidly that the σ-adducts cannot be detected. This is true both of the series of azines and of the anionic σ-complexes of aromatic polynitrocompounds.[43–46] When X = H, the σ-adducts formed are relatively more stable and nucleophilic substitution of hydrogen is then known to require an oxidant.[7,8] The knowledge of the conditions governing the formation of the σ-adducts and the choice of a suitable oxidant make it possible to achieve successfully reactions involving the nucleophilic substitution of hydrogen in the series of azines. A number of recently published studies on the low-temperature oxidation of the σ-adducts of azines with ammonia demonstrate how attractive and promising is this direct amination method.[32,47,48]

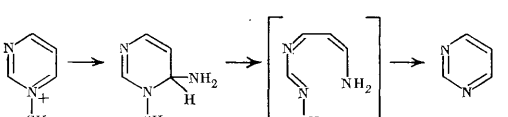
Another possible reaction pathway for the azine σ-adducts involves the opening of the heterocycle with subsequent formation of a new cyclic system; these are the so-called recyclisation reactions. The studies by Dutch chemists, namely van der Plas and co-workers,[4–6] have played a major role in the study of the recyclisation reactions of azines and other heterocyclic systems. These investigations showed that many outwardly simple nucleophilic substitution reactions of azines in reality proceed via the $S_N(ANRORC)$ mechanism.[4–6] The substitution of chlorine in 2-chloropyrazine on treatment with potassium amide in liquid ammonia can serve as an example of a reaction which takes place to the extent of 100% via the $S_N(ANRORC)$ mechanism:[49]



(I) (II)

Here and henceforth $\overset{*}{N}$ represents nitrogen enriched in the ^{15}N isotope.

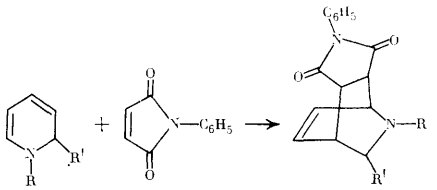
The observation of the demethylation of *N*-methylpyrimidinium salts in liquid ammonia[31] led to the concept of the so-called degenerate transformations of heterocycles,[5] i.e. reactions in which the initial heterocyclic system is restored as a result of recyclisation:



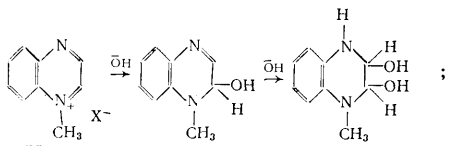
(III) (IV)

If the formation of the σ-adducts can be detected by NMR, then in the majority of studies on the recyclisation of azines[4-6] this is regarded as a stage preceding the opening of the heterocycle. The opening of the ring in the σ-adducts (I) and (III), formed in these and similar recyclisation reactions, is usually postulated on the basis of the results of experiments using ^{15}N isotope labels. It has been suggested[5] that the opening of the ring in the dihydropyrimidines (III) proceeds most probably as a thermally allowed $[\pi 4_s + \sigma 2_s]$-electrocyclic disrotary reaction. However, it must be emphasised that direct evidence for the involvement of the non-cyclic intermediates of type (II) and (IV) in the above reactions of the heterocycles has not so far been obtained.

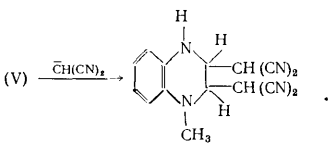
As regards the σ-adducts of azines, they have long ceased to be merely hypothetical intermediates. Studies whose authors were enabled by the knowledge of the structure and conditions of the formation of the σ-adducts to employ them as starting materials for further syntheses are being published at an increasing frequency. Examples of such an approach have been quoted in a review[50] devoted to advances in the chemistry of dihydropyridines. The addition of nucleophiles to pyridines and pyridinium salts is regarded in this review as one of the methods of synthesis of 1,2- and 1,4-dihydropyridines. The σ-adducts formed can be used further as the starting materials in [4 + 2]- and [2 + 2]-cycloadditions, *N*-alkylation and *N*-acylation reactions, and other transformations:[50]



Yet another reaction pathway involving the σ-adducts is the secondary addition of a nucleophile with formation of bis-adducts. The presence of electron-accepting groups in the aromatic ring creates in many instances a structural situation where the remaining double bond (or bonds) of the σ-adduct is activated for secondary nucleophilic attack. Among azines, the tendency towards the formation of bis-adducts is most characteristic of compounds containing the pyrazine ring: pyrazines,[51] quinozalines,[18,35,51,52] pyrido[2,3-*b*]pyrazines,[53-55] and pteridines.[37-39] Thus the quinoxalinium salts (V) combine twice with both heteroanions[35] and carbanions:[52]

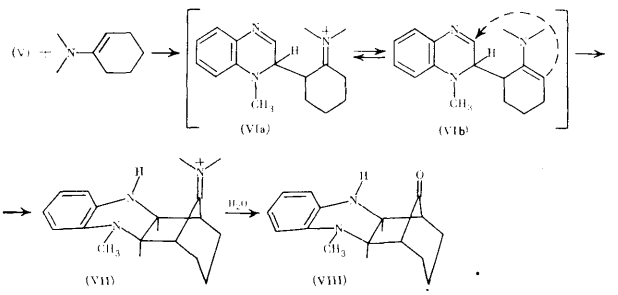


(V)



The bis-adducts formed in the reactions of pyrazines with heteroatomic nucleophiles usually exist in solution in equilibrium with the monoadducts, but are detected in the ^1H NMR spectra from the characteristic absorption of the H(2) and H(3) protons in the range 3.8–5.4 p.p.m. and the low values of the vicinal CSSI (Table 2). An important factor increasing the stability of the bis-adduct is the presence of an aromatic ring or an aromatic aza-ring condensed with the tetrahydropyrazine ring. It is not fortuitous that all the examples presented in Table 2 refer to bicyclic 1,4-diazines and the presence of a positive charge in the pyrazine ring in the initial substrates is not an obligatory condition for the formation of the bis-adducts (Table 2). Monocyclic pyrazines react with heteroatomic nucleophiles to form monoadducts (Table 1), but the more stable products of the addition of two *C*-nucleophile residues to pyrazines have been obtained on a preparative scale.[51] Bis-adducts with *C*-nucleophiles have also been obtained in the reactions of quinoxalinium[52] and pyrido[2,3-*b*]pyrazinium[53-55] cations.

It is readily seen that reactions involving diaddition to 1,4-diazines create conditions also for the formation of cyclic adducts when the reactant contains two nucleophilic centres. Thus, for example, the enamines derived from cyclic ketones, which exhibit the properties of 1,3-dicarbanionic reagents, react with quinoxalinium salts to form the cyclic adducts (VII) and (VIII):[59,60]



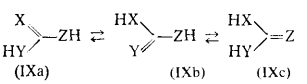
It has been suggested that the cyclisation takes place stepwise via a stage involving the formation of the σ-adduct (VI). Depending on the nature of the reactants, the reactions of azines with dinucleophiles can also proceed via other mechanisms (see below).

Bifunctional nucleophiles are usually classified in terms of the atoms which function as the nucleophilic centres (C,C-; C,N-; C,O-; N,N-; etc.) and also of their relative positions (1,2-, 1,3-, and 1,4-dinucleophiles). Analysis of the literature data shows that the 1,3-dinucleophiles are used most frequently because their cyclisations with azines lead to the formation of unstrained five- and six-membered rings.

In the present review an attempt has been made to summarise the data published during the last ten years on the cyclisations of azines with 1,3-dinucleophiles which make it possible to annelate to an aromatic aza-ring various carbocyclic and heterocyclic fragments; in addition, the cyclisation leading to *m*- and *p*-linked bicyclic adducts as well as the products of the transformation of azines under the influence of 1,3-dinucleophiles are examined.

III. 1,3-BIFUNCTIONAL NUCLEOPHILES

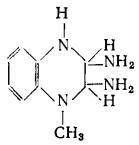
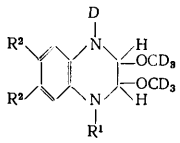
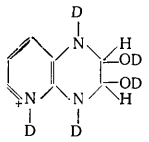
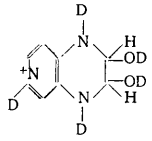
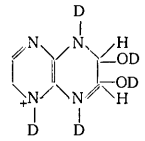
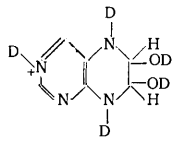
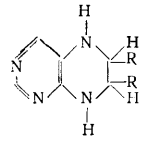
Ketones,[61,62] ketone enamines,[59,60,63,64] β-diketones and their derivatives,[65-71] ureas, thioureas, and guanidines,[72-74] amidines,[75,76] α-substituted acetamidines[76-79] and iminoesters,[80-82] CH-active acetamides,[70,74,83] and other reagents described by formulae (IX, a–c) have been used as 1,3-dinucleophiles in reactions with azines;



(IXa) (IXb) (IXc)

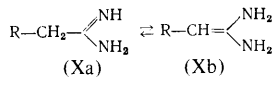
where X, Y, and Z are C-, N, O-, or S-substituted residues.

Table 2. ^{1}H NMR spectra of the diadducts of pyrazines with heteroatomic nucleophiles (δ = chemical shifts of the signals due to the protons of the tetrahydropyrazine ring).

Adduct	Solvent	δ, p.p.m.	CSSI, Hz	References
	NH_3 (liq.)	3.96; 4.07	$J_{2,3}=2.5$	[18]
 $R^1=CH_3$, $R^2=H$	CD_3OD	4.62(2H)	—	[35]
$R^1=C_2H_5$, $R^2=H$	CD_3OD	4.71(2H)	—	[36]
$R^1=CH_3$, $R^2=$ benzo-	CD_3OD	4.76(2H)	—	[36]
	D_2O	5.17; 5.28	$J_{2,3}=3.0$	[56]
	D_2O	5.07; 5.15	$J_{2,3}=3.0$	[56]
	D_2O	5.27(2H)	—	[56]
	D_2O	5.20; 5.35	$J_{6,7}=3.4$	[57]
 $R=NH_2$	NH_3 (liq.)	4.14; 4.20	—	[37]
$R=NHCH_3$	DMSO-d_6	3.83; 3.95	—	[58]

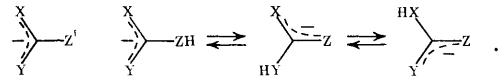
1. Tautomerism and Ambident Nature

A common structural feature of the 1,3-dinucleophiles considered is the presence of a double bond conjugated with a heteroatom having an unshared electron pair. A characteristic of such three-centre unsaturated systems is their capacity for prototropic tautomerism. The keto–enol,[84] thione–thiol, imino–enamine, lactim–lactam, and other types of triad tautomerism are known.[85] Certain types of tautomeric transformations, in particular, the existence of acetamidines (Xa) in the form of keten *N,N*-acetals (Xb), have been confirmed experimentally quite recently:[77,78]



(Xa) (Xb)

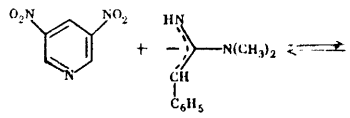
Many reactions of azines with 1,3-dinucleophiles take place only in the presence of bases. Tautomeric systems which exist solely in two forms give rise to the ambident anions (XI) on treatment with bases; in the case of three tautomeric forms, there is a possibility of the existence of the tautomeric anions (XII, a–c):

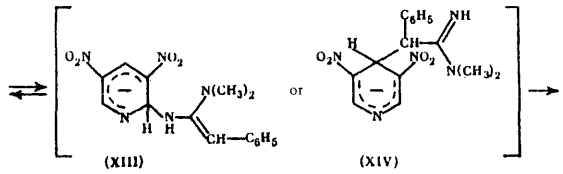


(XI) (XIIa) (XIIb) (XIIc)

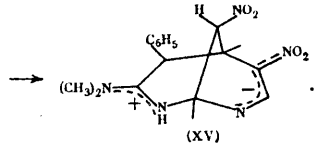
In the anions (XI) and (XII, a–c) the negative charge is distributed between the atoms of the triad and each of the terminal atoms can participate in the formation of a bond with the electrophile. Classical examples of 1,3-ambident anions are, for example, the enolates of β-diketones which form both *C*- and *O*-alkylation products.[86,87]

Thus the 1,3-ambident nature of nucleophiles combined with the behaviour of azines as polydentate species permits the formation of several types of mono-adducts which differ both in the site of the addition of the nucleophile to the azine nucleus and in the terminal atoms of the 1,3-anionic system involved in the formation of the bond. 1,3-Ambident systems are capable of reacting not only via each of its nucleophilic centres separately but also simultaneously via both such centres, which is the reason for the possibility of the formation of rings. Thus the reaction of 3,5-dinitropyridine with *N,N*-dimethyl-α-phenylacetamidine leads to the bridged cyclic adduct (XV)[88] and both the *N*- and *C*-adducts (XIII) and (XIV) can be regarded as probable intermediates:





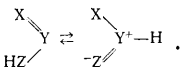
(XIII) (XIV)



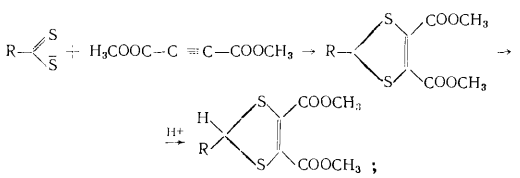
(XV)

2. Anionic and Dipolar Cycloaddition Reactions

It has been suggested in the literacture[89] that any triatomic systems of the type $\bar{Z}-X=Y$ and $\ddot{Z}-X=Y$, where Z is an atom with a free electron pair, are potential 1,3-dipoles. It has also been shown in a number of studies[90-94] that systems of the type X=Y−ZH are sources of 1,3-dipoles as a result of prototropic tautomerism:



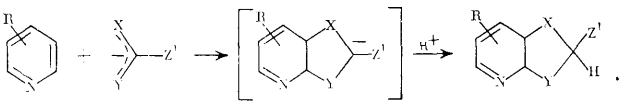
A number of studies have been published in recent years on the cycloaddition reactions with participation of heteroallyl anions.[68,69,80-82,95-108] For example, it has been found that the anions of dithiocarbamic[104] and also dithiocarbonic acid[101] react with a typical dipolarophile, namely dimethyl acetylenedicarboxylate, to form the 1,3-dithiols (XVI, a and b):



(XVI, a and b):

(a) R = $N(C_2H_6)_2$; (b) R = C_6H_5 .

Many of the dinucleophiles examined above conform to the principles, formuldted by Petrov et al.,[104] of the construction of systems capable of anionic cycloaddition. In the light of these requirements, we believe that the possibility of the concerted cycloaddition of 1,3-ambident anions to a double bond of the aromatic aza-system is entirely realistic.



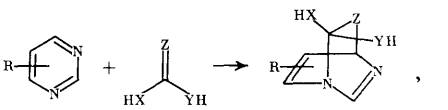
(XVII)

We shall consider the simplest case—the reaction of pyridine (pyridinium ion) with the 4π-electron heteroallyl system from the standpoint of the theory of molecular frontier orbitals.[109] The form of the highest occupied molecular orbitals (HOMO) of the heteroallyl anion and the lowest unoccupied molecular orbitals (LUMO) of the pyridinium cation, presented in the Figure, shows that the anionic cycloaddition at the C(2) and C(3) positions in the pyridine ring is prohibited owing to the phase incompatibility of the frontier orbitals but is possible at the C(3) and C(4) positions.

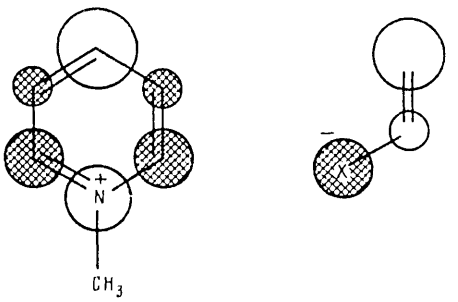
Apart from the limitations imposed by the theory of frontier molecular orbitals, the reaction via the anionic cycloaddition mechanism requires the stabilisation of the anionic intermediate (XVII), for example, as a result of protonation.[95] Furthermore, in the course of the anionic cycloaddition reactions the aromaticity of the azine ring is lost and the operation of this mechanism is therefore possible only for azines with an extremely low degree of aromaticity. Apparently, because of all these factors, clear-cut examples of anionic cycloaddition involving azines have not so far been found.

3. The Diels–Alder Reaction with Reverse Electronic Requirements

A number of 1,3-ambident nucleophiles contain a double bond enriched in electrons and can be regarded as 2π-components in reactions involving cycloaddition to the electron-deficient azadiene system of azines (the Diels–Alder reaction with reverse electronic requirements).[110,111] In a general form, such cyclisation can be described schematically as follows:



where XH and YH are electron-donating groups. Such reactions are at present known for azines containing at least two aza-groups in the *meta*-positions and yet another acceptor: nitropyrimidines, triazines, and tetrazines.



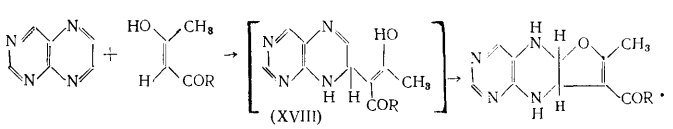
Schematic representation of the lowest unoccupied molecular orbital of the pyridinium cation and of the highest occupied molecular orbital of the heteroallyl anion.[109] The diameters of the circles are proportional to the coefficients of the atomic orbitals and cross-hatching indicates a change in the sign of the wave functions.

IV. THE CYCLISATION REACTIONS OF AZINES WITH 1,3-DINUCLEOPHILES

The reactions of azines with 1,3-dinucleophiles can in general lead to bicyclic systems with an *o*-, *m*-, or *p*-linked aza-ring. Despite a number of common features and the identity of the reagents capable of inducing all three types of cyclisation, the mechanisms of the formation of *o*-, *m*-, and *p*-linked cyclic adducts are different and merit separate consideration.

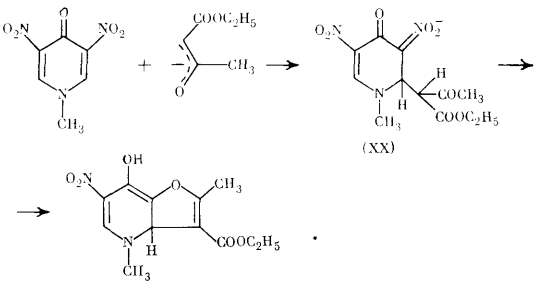
1. *ortho*-Cyclisations

One of the first examples of the *o*-cyclisations of azines with 1,3-dinucleophiles is the reaction of pteridine with β-dicarbonyl compounds.[71] The authors[71] suggested a stepwise cyclisation mechanism involving the intermediate formation of the monoadduct (XVIII). It is noteworthy that the structure of the cyclic adducts (XIX) has not been rigorously demonstrated and one cannot rule out the possibility of the reverse regio-orientation of the furan ring:



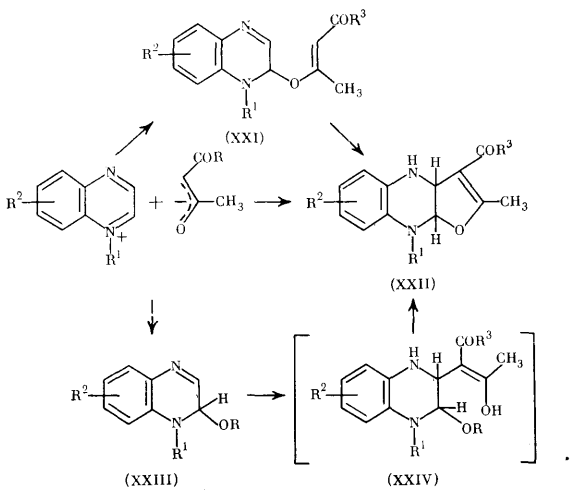
(XVIII) (XIX)

A similar mechanism with the initial formation of Michael adducts (XX) has also been proposed for the reactions of 3,5-dinitro-4-pyridone,[112] 3-bromo-4-nitropyridine *N*-oxide,[113] and 2,3,5,6-tetrachloropyrazine[114] with the anions of β-dicarbonyl compounds in which the furan ring is annelated as a result of the successive nucleophilic substitution of the halogen atoms or the nitro-group#:



(XX)

The mechanisms discussed in a number of studies[71,112-114] are inapplicable to the outwardly similar cyclisations of quinoxalinium salts with the enolates of β-dicarbonyl compounds in which the furan ring is also annealed but the C(2) atom, which is the most electrophilic in quinoxolinium salts, is linked during the reaction to the enolate oxygen. The reverse orientation of the furan ring presupposes either the initial formation of a C—O bond (charge control) in the stepwise course of the reaction via the σ-adduct (XXI) or the concerted formation of the C—O and C—C bonds via the anionic cycloaddition mechanism.[67-69] If the reaction is carried out in an alcoholic medium and is catalysed by bases, one cannot rule out also a mechanism in which the lyate complex (XXIII) is formed initially. Next there is a possibility either of the displacement of the OR group from the σ-adduct (XXIII) by the enolate anion, which leads to the formation of compound (XXI), or of the *C*-addition of the enolate to the 3-position. The complex (XXIII) can be detected in the ^{1}H NMR spectra and its conversion into the cyclic adduct (XXII) has been confirmed experimentally.[36]

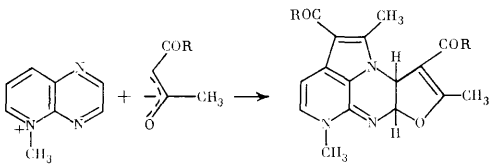


(XXI) (XXII) (XXIII) (XXIV)

#The cyclisations of azines with 1,3-dinucleophiles which take place as a result of the substitution of readily removed groups, as well as the cyclisations involving side groups, have their specific features and are not considered in this review.

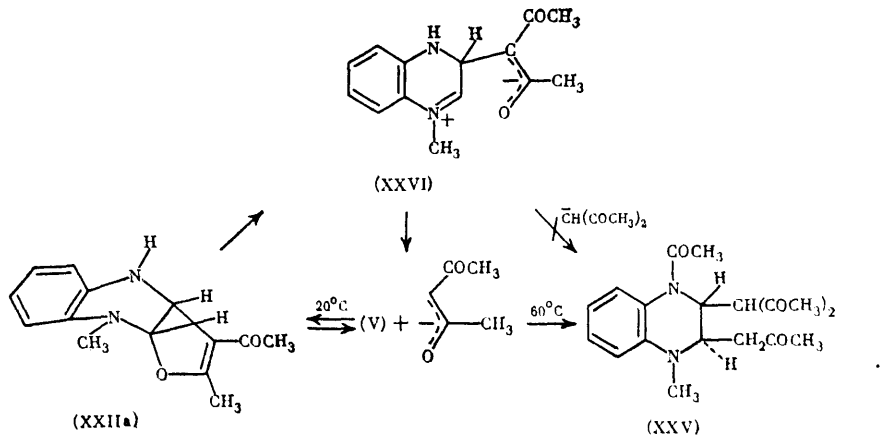
It has been shown by ^{1}H NMR and X-ray diffraction that, under the conditions of kinetic control, the reaction is highly regioselective and stereoselective and leads exclusively to the cyclic adducts (XXII) with the *endo*-configuration and *cis*-orientation of the bridgehead hydrogen atoms.[68] Quinoxalinium salts substituted in the benzene ring, including benzo[*g*]- and benzo[*f*]-annelated cations, react with the enolates to form cyclic adducts (XII) of analogous structure.[69]

The pyrido[2,3-*b*]pyrazinium cation reacts with the enolates in a more complex manner.[69] Apart from the annelation of the furan ring to the uncharged (as in pteridines[71]) pyrazine ring, in this case the second diketone residue undergoes *C*-addition to the *p*-position of the pyridinium ion with subsequent intramolecular cyclisation to the pyrrole ring:[69]

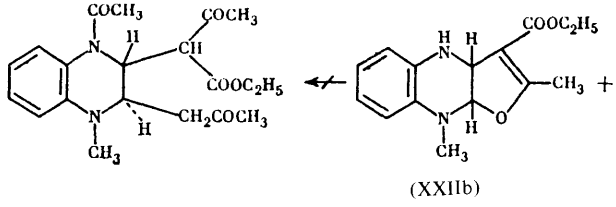


The question how the *o*-cyclisations discussed above take place—stepwise or as concerted pericyclic reactions—is common to these processes and is of fundamental importance. It is known[115-118] that the *cis*-principle is one of the main criteria of pericyclic reactions. The regiospecificity and stereospecificity of the cyclisation of β-diketones with aromatic 1,4-diaza-salts as well as their occurrence in conformity with the *cis*-principle constitute, as it were, arguments in support of anionic [3$^-$ + 2]-cycloaddition. However, it was noted above that the anionic cycloaddition at the C(2) and C(3) positions in the pyridinium ion is prohibited by the phase incompatibility of the frontier orbitals. Since it is difficult to expect a qualitative change in the properties of the LUMO on passing from the pyridinium to the pyrazinium (quinoxalinium) cation in view of their topological similarity, the question of the mechanism of the cyclisations considered remains open and requires both more profound quantum-chemical analysis and additional experimental data.

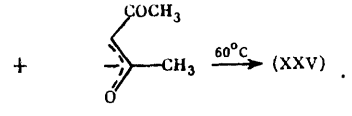
The experimental data demonstrating the concerted nature of the reverse cyclodecomposition reaction may serve as an additional argument in support of the concerted mechanism of the cyclisation of the enolates with quinoxalinium salts.[119] It has been shown that furo[2,3-*b*]quinoxaline (XXIIa) is formed only under the conditions of kinetic control at temperatures below 20 °C, but at 60 °C the reaction of *N*-methylquinoxalinium with acetylacetonate leads to the diadduct (XXV) with the *trans*-orientation of the hydrogen atoms located at the C(2) and C(3) atoms of the tetrahydropyrazine ring:[119]



Compound (XXV) is also formed when a solution of the cyclic adduct (XXIIa) in ethanol, heated to 60 °C, is treated with a second mole of acetylacetonate. The stepwise mechanism of this reaction via the intermediate (XXVI) in accordance with the scheme (XXIIa) → (XXVI) → (XXV) has been disproved by an experiment in which acetylacetonate was added at 60 °C to a solution of the cyclic adduct (XXIIb) having the ethoxycarbonyl group in the furan ring, which led to the diadduct (XXV) without the ester group:[119]



(XXIIb)

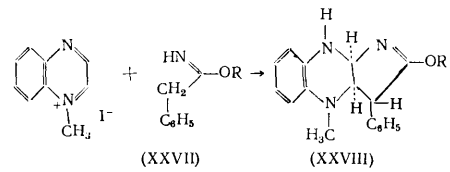


The result of this experiment demonstrates the reversibility of the cyclisation of the cation (V) with the enolates and also that the rupture of both σ-bonds (C–O and C–C) in the dissociation of the cyclic adduct (XXIIa) to give the starting materials most probably takes place via a concerted mechanism. The base-catalysed cycloreversions of tetrahydrofurans,[120] which have been discussed as concerted reactions,[118] constitute a fairly close analogy.

However, one cannot rule out fully the stepwise mechanism of the dissociation of the cyclic adduct (XXIIa) in accordance with the scheme (XXIIa) → (XXVI) → (V) + diketone. The absence of the reaction (XXVI) → (XXV), demonstrated by the experiment involving the transformation of compound (XXIIb) into (XXV), can be accounted for by the unduly short lifetime of the intermediate (XXVI) and its much faster dissociation compared with the rate of addition of the second diketone residue.

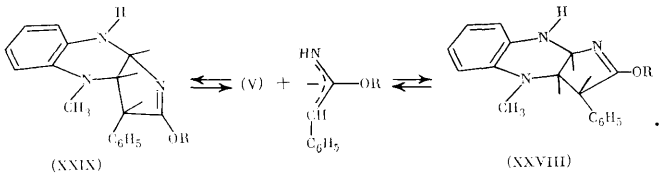
It is noteworthy that the cyclisation reactions of pyrazines with β-ketoenolates merit attention as a method of synthesis of furo[2,3-*b*]pyrazines regardless of the mechanism.

The annelation of the pyrrole ring to pyrazines is achieved in the reactions with N, C-dinucleophiles such as α-substituted acetiminoesters (XXVII),[80–82] acetamides, and β-ketoacid amides:[121]



(XXVII) (XXVIII)

Under the conditions of thermodynamic control, the interaction of quinoxalinium salts with iminoesters takes place regioselectively and stereoselectively and leads to the cyclic adduct (XXVIII) having the *exo*-structure.[81] In base catalysis the rate of cyclisation increases and two types of stereoisomeric cyclic adducts (XXVIII) and (XXIX) have been detected in the reaction mass by ^{1}H NMR. They have also been isolated on the preparative scale in the form of crystals:[80]

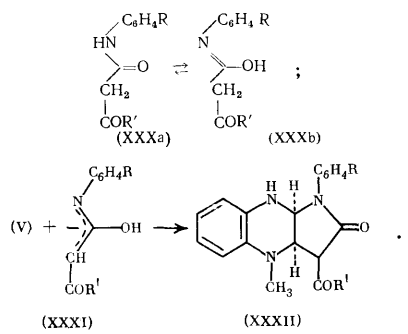


(XXIX) (XXVIII)

It has been shown chemically and spectroscopically that the *endo*-adducts (XXIX) are formed at a high rate in the initial period but under the reaction conditions the *endo*-adducts rearrange irreversibly to the more stable *exo*-isomers (XXVIII). It has been established that the rearrangement proceeds via a cycloelimination stage, i.e. via the decomposition of the *endo*-isomers to the starting materials.[80]

The above characteristics of the cyclisation of quinoxalinium salts with iminoesters repeat in broad outline the characteristics of the cycloaddition reactions[115–118] and, in particular, the anionic cycloaddition reactions.[95,97] It therefore appeared quite justifiable to regard these reactions as anionic [3$^-$ + 2]-cycloaddition of heteroallyl anions to the conjugated C=C bond of the pyrazine ring.[80]

The anilides of β-ketoacids (XXX) in the potentially tautomeric form (XXXb) are in essence analogues of iminoesters. They too react with quinoxalinium salts (V) to form the cyclic adducts (XXXII) containing the pyrrole ring:[121]

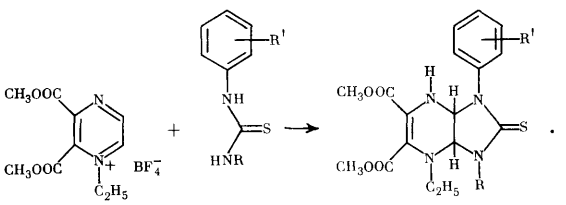


(XXXa) (XXXb)

(XXXI) (XXXII)

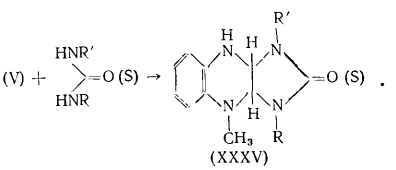
The high regioselectivity and stereoselectivity of the cyclisation is noteworthy. Despite the fact that the mesomeric anion (XXXI) participates in the reaction, no appreciable amounts of furo[2,3-*b*]quinoxalines or other cyclic adducts are formed.[121]

The annelation of the imidazole ring, leading to derivatives of imidazo[4,5-*b*]pyrazine (XXXIV), takes place in the reactions of pyrazinium salts with *N*-mono- and *N*,*N*′-di-aryl-substituted thioureas (XXXIII):[122]



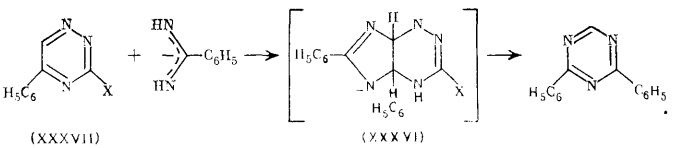
(XXXIII) (XXXIV)

Ureas and thioureas also behave as N,N′-dinucleophiles in reactions with quinoxalinium salts (V), giving rise to the products (XXXV):[122]



(XXXV)

The bicyclic adducts (XXXVI) with the annelated imidazole ring have also been regarded as the most probable intermediates in the transformation of 1,2,4-triazines (XXXVII) into 2,4-diphenyl-1,3,5-triazine, which has a fairly complex mechanism:[123]



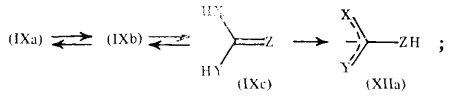
(XXXVII) (XXXVI)

We may mention again that the presence of the pyrazine fragment in the triazines (XXXVII) is structurally favourable for *o*-cyclisations.

A characteristic feature of the ^{1}H NMR spectra of all the cyclic adducts of pyrazinium and quinoxalinium salts with 1,3-dinucleophiles mentioned above is fairly high values of the vicinal CSSI between the protons at the bridgehead carbon atoms (^3J = 7–10 Hz), which indicates a *cis*-junction between the five-membered heterocycles and the pyrazine ring.[68,69,80,81,121,122]§ As already mentioned above, other vicinal constants $^3J_{2,3}$ = 2.5–3.5 Hz (Table 2), corresponding to the *trans*-orientation of the protons in the tetrahydropyrazine ring, are characteristic of the acyclic diadducts of pyrazines and quinoxalines.

If an attempt is made to formulate the empirical principles of the selection of 1,3-dinucleophiles (IX) capable of *o*-cyclisation, it is found that a common feature of different combinations of the heteroatoms X and Y remains, on the one hand, the presence of substituents stabilising the 1,3-ambident anions (XIIa) formed (this is frequently the phenyl or keto-group) and, on the other hand, the presence at the central atom of a triad of electron-donating groups of the type NR_2, OR, SR, or the methyl group, which activate these systems with respect to interaction with electron-deficient azines.

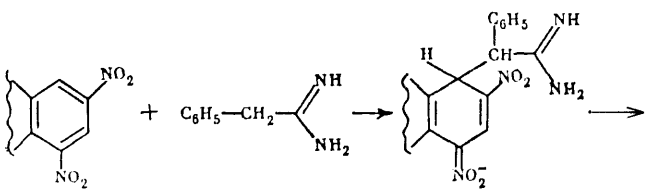
§ The ^{1}H NMR spectra of tetrahydroquinoxalines condensed with five-membered heterocycles have been discussed in detail by V.N.Charushin, A.I.Chernyshov, N.N.Sorokin, and O.N.Chupakhin, Org.Magnet.Resonance, 1984 (in the Press).



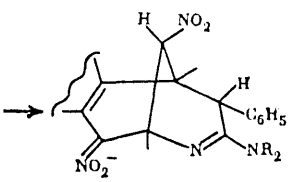
X, Y = N, O, S, CH, NH, NAr, CHAr, CHCOR;
ZH = NR_2, OR, SR.

2. *meta*-Cyclisations

The characteristic features of *m*-cyclisations with 1,3-dinucleophiles were first formulated clearly by Strauss in a series of studies of the reactions of aromatic polynitro-compounds with enamines, α-phenylacetamidines, and urethanes:[124-130]



(XXXVIII)

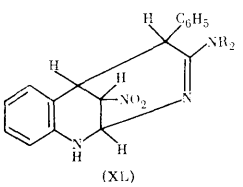


(XXXIX)

Cyclisations of this type, which have been called *meta*-bridging reactions,[124] immediately attracted attention as a direct and convenient method of synthesis of complex polycyclic structures. In particular, Strauss[126] demonstrated the applicability of these reactions to the direct synthesis of benzomorphans—potential antagonists of narcotic drugs.

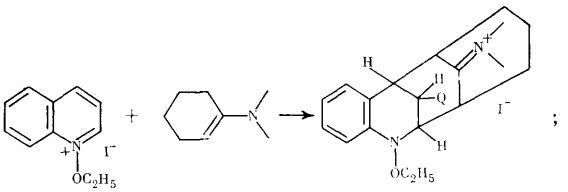
It has been suggested[124] that *m*-cyclisations take place in two stages via the intermediate formation of the anionic σ-complexes (XXXVIII), which can not only be detected spectroscopically but in a number of instances can be isolated, after which the second stage of the reaction can be carried out—the cyclisation of the σ-complexes (XXVIII) to *m*-linked cyclic adducts (XXXIX).[130]

The *m*-bridging reactions were subsequently extended to the aza-analogues of aromatic polynitro-compounds such as 3,5-dinitropyridine and 3-nitroquinoline.[88]



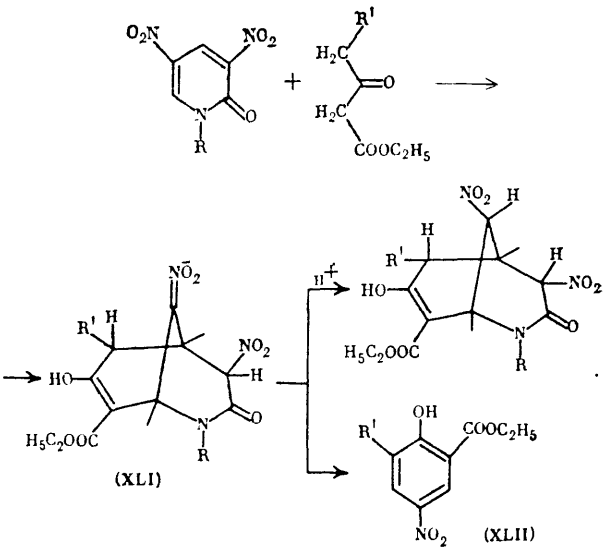
(XL)

The formation of the cyclic adducts (XV) and (XL) has been detected by ^{1}H NMR, but they could not be isolated.[88] This is due to the lower stability of the *m*-linked adducts of azines with 1,3-dinucleophiles compared with their nitro-analogues or with the *o*-annelated azines. In addition, the *m*-adducts undergo various chemical reactions. Thus the *m*-cyclisation of *N*-ethoxyquinolinium salts with enamines is accompanied by the addition of a second molecule of the initial cation:[61,64]



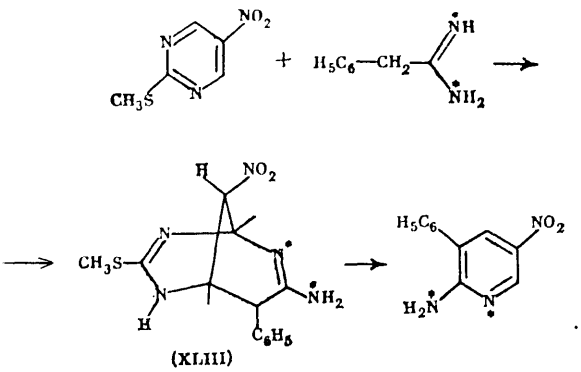
Q = 2-quinolinyl.

However, the most common reactions of the cyclic *m*-adducts are apparently their transformations into other heterocyclic systems. The sodium salts of β-ketoesters, for example, induce the transformation of 3,5-dinitropyridones into the nitrophenols (XLII) via the intermediate formation of bicyclic adducts (XLI), which can also be isolated on acidification of the medium:[66]



(XLI) (XLII)

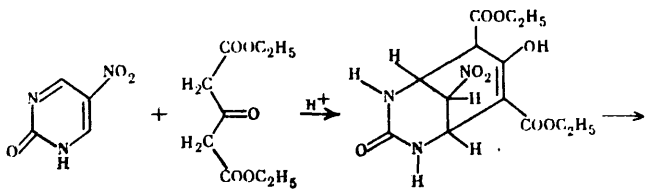
The formation of *m*-linked adducts has been postulated also in the transformation of 5-nitropyrimidines on treatment with the carbanions of keto-reagents[62] and also acetamidines[76]; however, experimental data confirming the feasibility of this mechanism of the transformation have been obtained quite recently.[78]



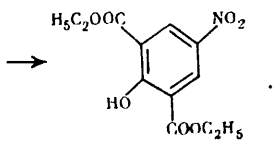
(XLIII)

The formation of the cyclic *m*-adducts (XLIII) in the reaction of 2-methylthio-5-nitropyrimidine with α-phenylacetamidine has been detected by ^{1}H NMR and its involvement in the rearrangement is not inconsistent with experimental data obtained using [^{15}N]amidine.[78]

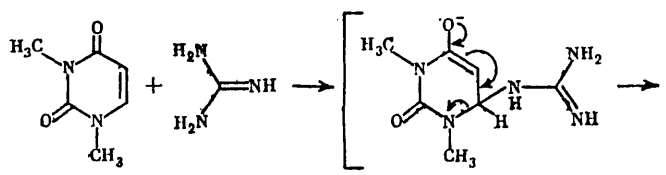
The involvement of bridged *m*-linked cyclic adducts (XLIV) in the transformations of 5-nitro-2*H*-pyrimidinone into nitrophenols on treatment with keto-reagents has been recently reported:[61]

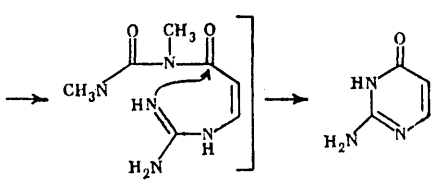


(XLIV)



We may note that earlier in the majority of their investigations of similar transformations of uracils under the influence of 1,3-ambident nucleophiles American and Japanese chemists were inclined to adopt the *ANRORC* mechanism involving an acyclic intermediate of type (XLV):[70,72-74]



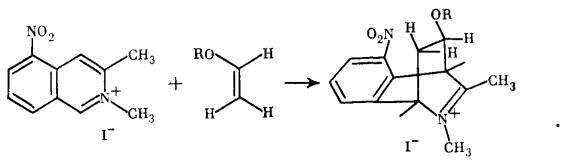


(XLV)

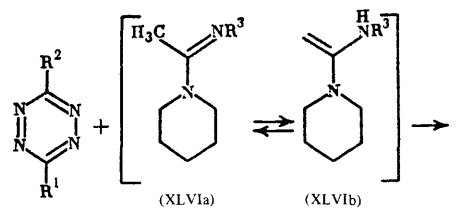
The question of the mechanism of the transformations of pyrimidines under the influence of 1,3-dinucleophiles still remains open, although studies in recent years have shown that the formation of bridged bicyclic intermediates in such reactions is extremely real.[61,66,78] Whereas the bridged cyclic adducts can nevertheless be detected in a number of instances,[61,66,78] the difficulties associated with the detection of the σ-adducts of azines with 1,3-dinucleophiles and even more so of the acyclic intermediates are evident. The σ-adducts formed on monoaddition of a 1,3-dinucleophile to azines with the *meta*-disposition of the electrophilic carbon atoms are extremely unstable, because their further reactions are greatly favoured by thermodynamic factors: they involve either the opening of the ring with rapid recyclisation or *m*-cyclisations with subsequent decomposition of the bridged cyclic adduct, leading to the transformation products.

3. *para*-Cyclisations

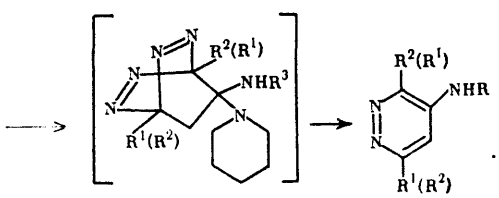
The most widely used method of synthesis of bicyclic systems with a bridge connecting the *p*-positions in the initial azine ring is the Diels–Alder reaction with reverse electronic requirements, in which the 4π-electron fragment of the azine system plays the role of the diene, while a wide variety of unsaturated compounds containing a double bond enriched in electrons are employed as dienophiles.[110,111] In conformity with the predictions of the theory of frontier orbitals, cyclisations of this type become energetically favourable only when several aza- or other electron-accepting groups have accumulated in the azine molecule or in the presence of a cationic centre, which all adequately reduce the energies of the lowest unoccupied molecular orbitals.[109,110,111,118] Derivatives of 1,2,4-triazine and 1,2,4,5-tetrazine,[111,131] as well as isoquinolinium and acridizinium cations, which readily enter into the cationic [4⁺ + 2]-cycloaddition reactions,[132-142] therefore show an extremely great tendency towards the formation of cyclic [4 + 2]-adducts:



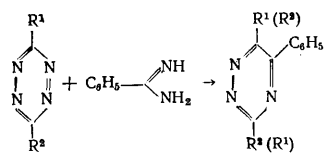
Many 1,3-ambident nucleophiles contain an electron-enriched double bond capable of participating in cycloaddition reactions with azadienes. Although there is no point in this connection to consider the manifestation of ambident properties by nucleophiles, these reactions nevertheless should be regarded as constituting another possibility for the involvement of 1,3-ambident systems in reaction with azines. This is particularly valid because the mode of many cyclisations is determined by tautomeric transformations characteristic precisely of 1,3-ambident systems and impossible in the case of isolated double bonds. Thus the acetamidines (XLVI) enter into reactions involving cycloaddition to tetrazines in the form of the enediamines (XLVIb) and it has been noted that the participation of acetamidines as C=C dienophiles is the first experimentally observed manifestation of the acetamidine–enediamine tautomerism.[77]



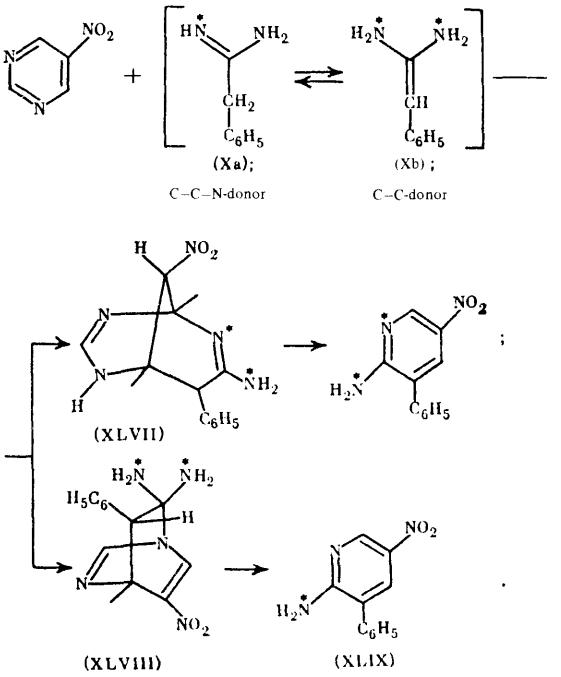
(XLVIa) (XLVIb)



In the absence of N,C-prototropic tautomerism, which obtains only in the presence of an active α-methylene group, amidines are capable of cyclising with tetrazines as C=N dienophiles:[143]

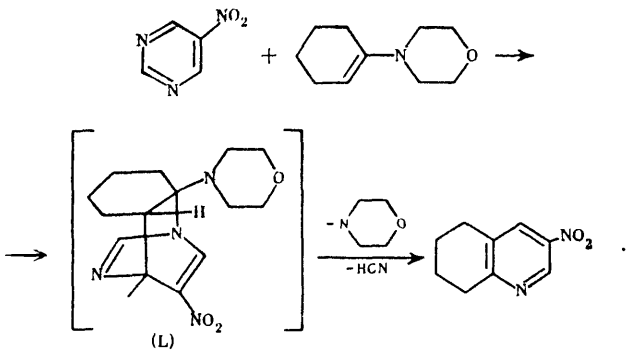


In some cases amidines are capable of exhibiting in their reactions with azines both the properties of 1,3-dinucleophiles and the functions of reverse dienophiles. It has been shown with the aid of ^{15}N isotope labels that the transformations of 5-nitropyrimidines on treatment with α-phenylacetamidines proceed via several mechanisms involving the formation of both bridged *m*-linked intermediates (XLVII) and *p*-linked cyclic adducts (XLVIII):[78]

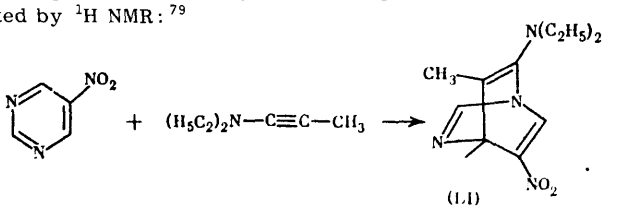


In the latter case the electron-enriched C=C bond of the enediamine (Xb) participates in the cyclisation, the enediamine thus behaving as a donor of the C–C fragment to the final transform5tion product, namely the pyridine (XLIX), which does not contain the ^{15}N isotope label in the ring.[78]

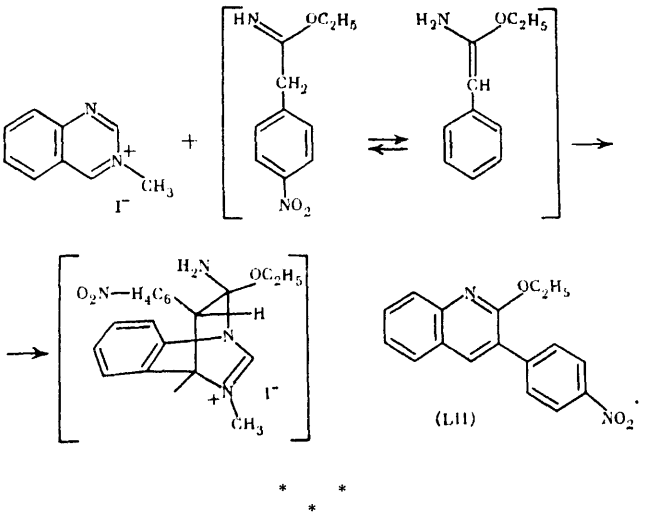
The transformations of pyrimidines based on the Diels–Alder reactions with reverse electronic requirements have been further confirmed and developed in a study[79] of the transformations of 5-nitropyrimidine on treatment with keten *O,O*- and *N,N*-acetals, enamines, and ynamines:



The postulated intermediates in these transformations, namely cyclic [4 + 2]-adducts of type (L), are unstable; on the other hand, in the case of *N,N*-diethylaminopropyne the stable cyclic adduct (LI) is formed as a result of addition to the 1,4-positions of the pyrimidine ring and has been detected by ^{1}H NMR:[79]

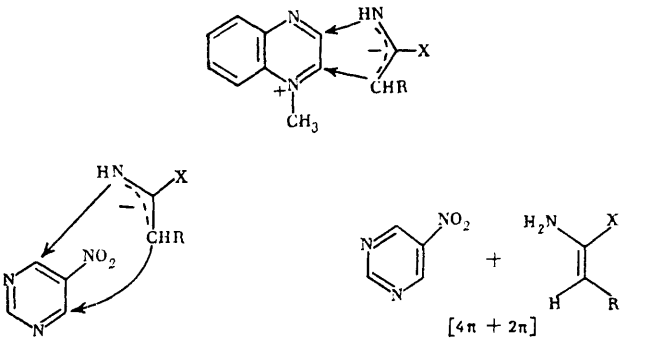


It is noteworthy that, whereas the formation of cyclic [4 + 2]-adducts with a *p*-linked 1,2,4-triazine or 1,2,4,5-tetrazine ring as intermediates in the transformations of the latter into other azine systems is generally accepted.[111,131] Charushin and van der Plas[78,79] were the first to conclude that systems with two heteroatoms can also participate in transformations proceeding via cyclic [4 + 2]-adducts. This result provides a more reasonable explanation of the previously described transformations of quinazolinium salts into the quinolines (LII) on treatment with methyl *p*-nitrophenylacetimidate[82] without resorting to open-chain intermediates and to *ANRORC* mechanisms usually postulated in such cases. This has been considered by Chupakhin et al.[82]



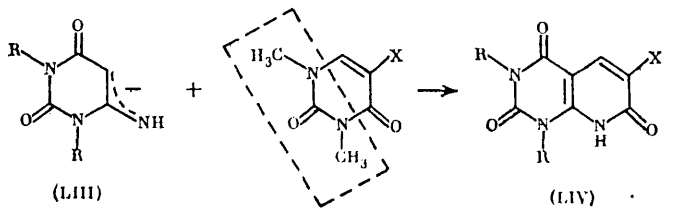
* * *

Thus the reactions of azines with ambident 1,3-nucleophiles are extremely varied and proceed via different pathways determined by the nature of the reactants, the structural and electronic factors, and the reaction conditions. The examples examined above show that, in reactions with ambident C,N-nucleophiles, such as, for example, acetamidines (acetimidates), there is a possibility of the formation of all three types of cyclic adducts: *ortho*-, *meta*-, and *para*-, the last two types of adducts being unstable and leading to the formation of transformation products.



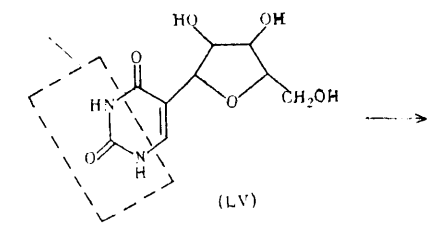
The data of Chupakhin et al.[82] for the reactivities of four isomeric benzodiazinium cations, namely quinoxalinium, cinnolinium, phthalazinium, and quinazolinium, with respect to *p*-nitrophenylacetimidate demonstrate a specific character of the *o*-, *m*-, and *p*-cyclisations rather than their common features.

The knowledge of the characteristics of the reactions of azines with ambident 1,3-nucleophiles and of the features of their occurrence in structurally different series of azines makes it possible to design new syntheses of azine systems and of annelated heterocycles based on them. Examples of such specific employment of cyclic ambident 1,3-nucleophiles (LIII) in the syntheses of pyrido[2,3-*d*]pyrimidines (LIV) have been described.[144,145] In the example presented in the scheme below the N–C–N fragment of 1,3-dimethyluracil is substituted by the C–C–N group of the 1,3-dinucleophile:[144]

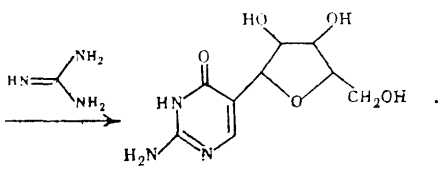


(LIII) (LIV)

A striking example of the practical use of the transformations of azines under the influence of 1,3-dinucleophiles has been given in a study[72] in which degenerate transformations of the pyrimidine ring were used for the modification of pyrimidine nucleosides. Thus pseudouridine (LV) can be converted under the influence of guanidine into pseudoisocytidine (LVI), which exhibits antileukaemic activity:[72]



(LV)



(LVI)

Further investigations of the cyclisation reactions and the transformations of azines on treatment with 1,3-dinucleophiles will make it possible to develop new easy methods of synthesis of practically useful compounds.

During the preparation of the manuscript for the press, a further series of studies on the cyclisation and transformations of azines under the influence of bifunctional 1,3-nucleophiles were published.[146–152] Among these, mention should be made of a novel one-stage method of synthesis of the familiar antitumour preparation 5-fluorouracil based on the transformation of 1,3-dimethyl-1,3,5-triazine-2,4-dione on treatment with fluoroacetamide.[147] This method undoubtedly merits attention, because transformations of this type can find applications also in the syntheses of other fluorinated heterocyclic compounds. We may also mention a review[150] of the Diels–Alder reactions of azadienes, which contains many examples of the participation of electron-deficient azines in cyclisations involving the *p*-position in the azine ring.

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Korov Urals Polytechnic
Institute, Sverdlovsk

Translated from *Uspekhi Khimii*, 53, 1675-1708 (1984) U.D.C. 547.241

The Reactivity of Organosilicon Derivatives of Phosphorus in Addition Reactions

G.A.Kutyrev and R.A.Cherkasov

The results of studies of the reactivity of organosilicon derivatives of tricoordinate and tetracoordinate phosphorus containing the P-X-Si (X = O, N, or S) groups in reactions involving addition to various unsaturated systems are examined and surveyed. Attention has been concentrated on the elucidation of the specific influence of the trialkylsilyl group on the character of the reaction of phosphorus-silicon compounds.
The bibliography includes 137 references.

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II. Organosilicon derivatives of tervalent phosphorus 971
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I. INTRODUCTION

During the last one and a half decades, organosilicon derivatives of phosphorus have been vigorously investigated in many world laboratories. The interest in these compounds is caused primarily by the possibility of synthesising on their basis a wide range of new organoelemental structures, many of which have important practical applications. The combination of phosphorus and silicon atoms in a single molecular system has its specific manifestation in the character of the chemical behaviour of phosphorus–silicon reagents, which differs from that of the corresponding organophosphorus or organosilicon analogues. The determination of the interrelation between the structure and chemical reactivity of such two-element compounds and the elucidation of the specific role of the phosphorus- and silicon-containing fragments in the molecule are of undoubted theoretical interest for organoelemental chemistry.

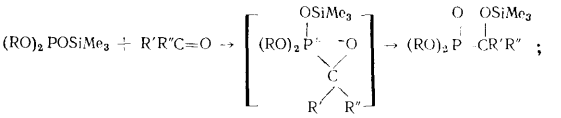
In the literature there are almost no reviews devoted to the reactivity of phosphorus–silicon compounds. Data concerning the synthesis of organosilicon derivatives of phosphorus and certain reactions of silyl phosphites, which may be used for the synthesis of phosphorus compounds, are summarised in the monograph of Voronkov and co-workers[1] and in publications of Japanese investigators.[2]

The present review deals with the reactivity of organosilicon derivatives of tervalent and quinquevalent phosphorus containing the P–X–Si group (X = O, N, or S) in addition reactions. Wherever possible, the reactivities of silylated phosphorus systems and phosphorus compounds of analogous structures without organosilicon groups have been compared in order to discover the factors which control the processes under discussion.

II. ORGANOSILICON DERIVATIVES OF TERVALENT PHOSPHORUS

1. Reactions with Aldehydes and Ketones

The silyl esters of tervalent phosphorus acids readily add to the carbonyl groups of aldehydes and ketones with formation of α-trialkylsiloxyalkylphosphonates:[3-10]

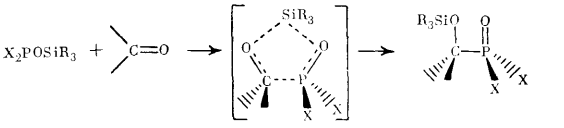


(I)

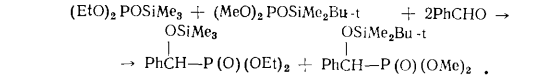
R' = Alk, Ar; R'' = H, Alk, Ar.

It has been suggested[6,9-11] that the reaction begins with nucleophilic attack by the phosphorus atom on the carbonyl carbon atom with formation of an intermediate dipolar ion (I). This mechanism is supported by the fact that the more nucleophilic trimethylsilyl dibutylphosphinite adds to acetaldehyde more readily than trimethylsilyl diethyl phosphite and the interaction of the same phosphinite with trifluoroacetone proceeds much faster than with acetone.[9]

At the same time, in contrast to trialkyl phosphites,[12] for phosphorus–silicon reagents one cannot rule out the possibility of a concerted 1,2-addition mechanism,[10] because the trialkylsilyl group can migrate as a result of frontal substitution at the silicon atom with retention of its configuration:[13,14]



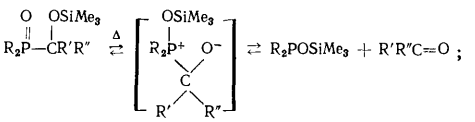
The results of a "cross-experiment" with participation of equimolar amounts of diethyl trimethylsilyl phosphite, t-butyldimethylsilyl dimethyl phosphite, and two equivalents of benzaldehyde confirm the intramolecular character of the migration of the silicon atom:[10]



With increasing steric hindrance at the silicon atom, the rate of addition diminishes under these conditions. The insertion of trialkyl phosphites in the carbonyl group takes place as a result of intermolecular alkyl transfer.[12]

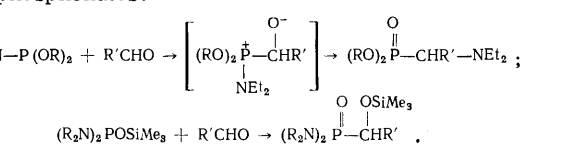
The adducts obtained by the interaction of silyl phosphites with aromatic aldehydes and ketones are thermally unstable and decompose on heating into the initial compounds.[15] The decomposition of α-trimethylsiloxyphosphonates via a pathway which is the reverse of the

Arbuzov reaction is accelerated with increasing nucleophilicity of the phosphoryl oxygen and with enhancement of the polarisation of the Si–O bond as a result of the electron-accepting influence of the substituents at the α-carbon atom:

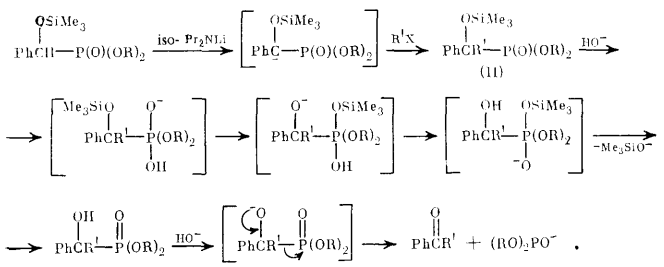


R=Bu, MeO, EtO; R′=H, Me; R″=Ph, COOEt, P(O)(OMe)$_2$.

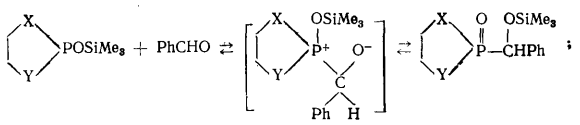
In contrast to dialkyl phosphoramidites, which react with aldehydes to form α-aminophosphonates,[16] trimethylsilyl *N,N,N′,N′*-tetra-alkylphosphorodiamidites give α-trimethylsiloxyphosphonates:[11,17,18]



The adducts of silyl phosphites with aldehydes have been recently used widely in the synthesis of asymmetric ketones.[19–21] The ready dissociation of the P–C bond in compound (II), obtained by alkylating the comparatively acidic α-hydrogen atom in α-trimethylsiloxybenzylphosphonate, is promoted by the sigmatropic migrations of the Me_3Si group in the course of the nucleophilic attack by the hydroxide anion on the phosphorus atom:



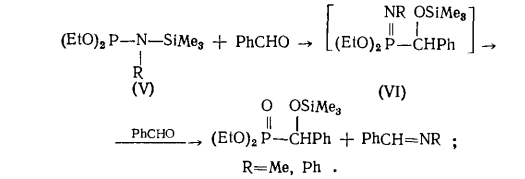
The P–N bond is cleaved and 1,4,2-oxazaphosphorinanes are formed on interaction of 2-alkoxy(alkyl)-1,3,2-oxazaphospholans with carbonyl compounds.[22] In contrast to this, the cyclic fragments are retained in the reactions of 2-siloxy-derivatives of 1,3,2-diheterophospholans with benzaldehyde. The reaction is reversible and on heating α-trimethylsiloxyphosphonate decomposes into the starting materials:[23]



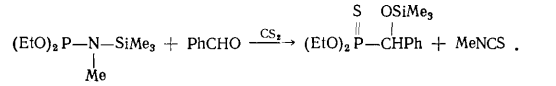
(a, X=Y=O; (b) X=NMe, Y=O; (c) X=NPh, Y=O; (d) X=Y=NBu .

Two versions of the relative orientations of the benzaldehyde and oxazaphospholan molecules in the intermediates (III, b and c) determine the formation of diastereoisomeric cyclic α-trimethylsiloxybenzylphosphonates (IV).

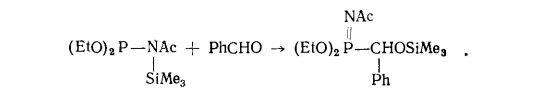
The interaction of phosphorous acid *N*-trimethylsilylamides (V) with benzaldehyde proceeds differently.[24,25] The phosphonimidate (VI), formed as a result of the nucleophilic addition of the phosphoramidite to the carbonyl group, reacts vigorously with a second benzaldehyde molecule, which leads to α-trimethylsiloxybenzylphosphonate and benzylideneamine:



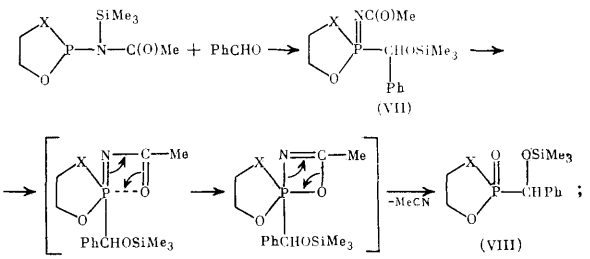
In the presence of carbon disulphide the intermediate phosphonimidate (VI) is converted into a phosphonothioate:[24]



The introduction of the electron-accepting acetyl group at the nitrogen atom of *N*-silylphosphoramidite stops the reaction at the stage of the formation of the phosphonimidate:[23]



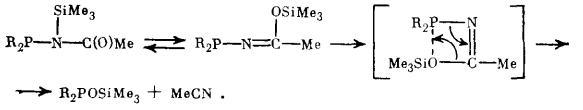
In the case of 2-(*N*-trimethylsilylacetamido)-1,3,2-diheterophospholans the reaction with benzaldehyde leads to the formation of the cyclic α-trimethylsiloxybenzylphosphonate:[23]



X=O, NMe .

The process involves the initial formation of *N*-acetylphosphonimidates (VII), which are converted into the phosphonates (VIII) by nucleophilic attack by the carbonyl oxygen at phosphorus. The ease of the intramolecular rearrangement depends significantly on the nature of the substituents at the phosphorus atom. In the series of 1,3,2-diheterophospholans the replacement of oxygen in the ring by the more electron-donating nitrogen reduces the electrophilicity of the phosphimide phosphorus and thereby stabilises the phosphonimidate structure (VII) (X = NMe). The interaction of 3-methyl-2-(*N*-trimethylsilylacetamido)-1,3,2-oxazaphospholan with benzaldehyde leads to the phosphonimidate (VII), which is stable under the usual conditions and is converted on heating to 65 °C into the phosphonate (VIII). In the series of dioxaphospholan derivatives (X = O) the phosphonimidate cannot be detected even at a low temperature.[23] A similar rearrangement of diethyl α-trimethylsiloxybenzylacetylphosphonimidate has been achieved only at 135 °C.

Acetyl and trimethylsilyl substitution at the nitrogen atom reduces significantly the thermal stability of the phosphoramidite. The migration of the Me_3Si group in *N*-acetyl-*N*-trimethylsilylphosphoramidite to the carbonyl oxygen promotes intramolecular nucleophilic substitution at the phosphorus atom and the formation of silyl phosphites and acetonitrile:[26,27]



The decomposition of *N*-silylated acetamido-derivatives of tervalent phosphorus depends on the nature of the substituents R at the electrophilic centre and, according to the results of the differential thermal analysis, is retarded with increase of their electron-donating capacity[27] (Table 1).

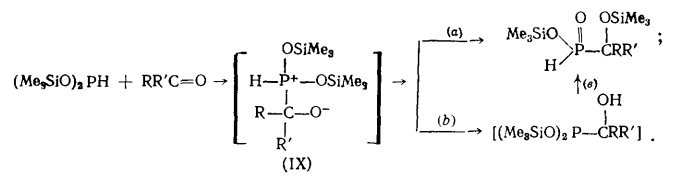
Table 1. The effect of substituents at the phosphorus atom on the rate of decomposition of the compounds $R_2P-N-SiMe_3$.[27]

	AC	
R_2	T_i, °C	T_m, °C
$-OCH_2CH_2O-$	35	88
$-OCH_2CH_2CH_2O-$	52	128
$-OCH_2CH_2N(Ph)-$	65	108
$-OCH_2CH_2N(Me)-$	70	130
$(EtO)_2$	95	135
Et_2*		

Notation: T_i is the temperature of the onset of the effect and T_m is the temperature of the maximum effects.

*Stable up to 200 °C.

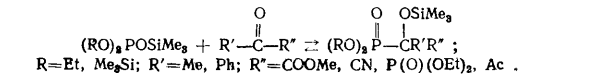
The addition of bis(trimethylsilyl) hypophosphite to aldehydes and ketones leads to bis(trimethylsilyl) alkylphosphonites with the retention of the P–H bond.[28,29] The dipolar ion (IX) formed initially can be stabilised by the migration of the Me_3Si group, which leads to the final reaction product [pathway (*a*)]; there is also a possibility of the intramolecular proton transfer [pathway (*b*)] and subsequent rearrangement of the intermediate bis(trimethylsilyl) α-hydroxyalkylphosphonite via pathway *c*:[29]



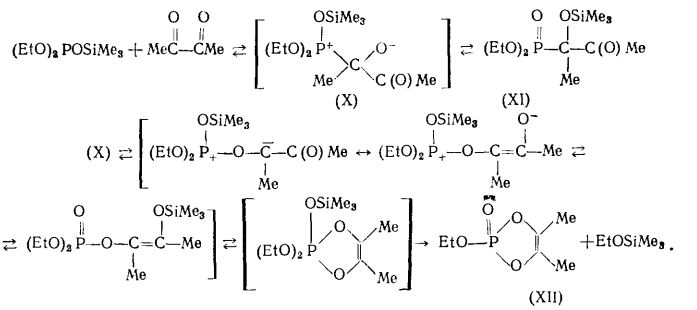
2. The Interaction with Carbonyl Compounds Containing Electron-Accepting Substituents

The introduction of electron-accepting substituents at the carbonyl group not only increases the reactivity of the carbonyl compounds in reactions with organosilicon derivatives of tervalent phosphorus but also in many cases influences significantly the mode of their interaction.

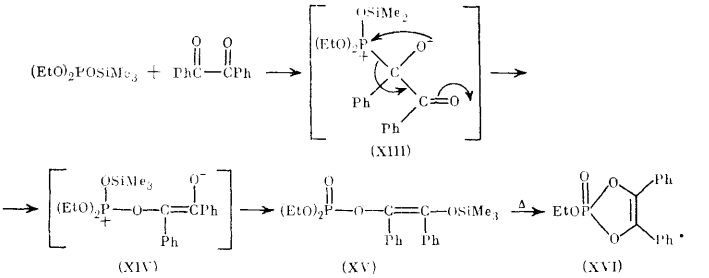
Silyl phosphites add vigorously to the esters and nitrile of pyruvic acids,[30] acetyl phosphonates,[31] benzoyl phosphonates,[32] and diacetyl[33–35] with formation of the corresponding α-trimethylsiloxyphosphonates:



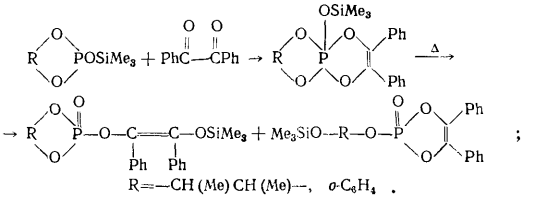
These reactions are as a rule reversible. However, after prolonged heating of the adducts, other processes can also occur. Thus, dioxaphospholen (XII) and ethoxysilane (XXXV) are formed from diethyl trimethylsilyl phosphite and diacetyl as a result of silotropic transformations and the phosphonate–phosphate rearrangement:[35]



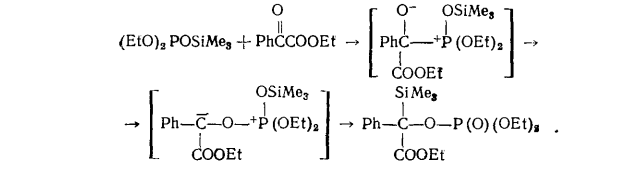
The dipolar intermediate can be stabilised by the intramolecular transfer of the trimethylsilyl or phosphoryl group. The ratio of the rates of these competing processes depends on the structure of the carbonyl reagent. For the diacetate, the α-siloxyphosphonate (XI) is the kinetically controlled product. In the reactions of silyl phosphites with benzil the phosphonate–phosphate rearrangement (XIII) → (XIV) is faster than the migration of the silyl group and the only product of the interaction is 2-trimethylsiloxy-1,2-diphenylvinyl phosphate (XV), which is converted into the dioxaphospholen (XVI) on heating:[34,36]



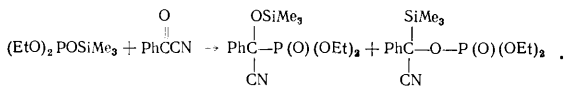
The formation of spiro-phosphorane structures, which is characteristic of the interaction of 1,3,2-diheterophospholans with dicarbonyl compounds,[37,38] is also observed in the reaction of 2-trimethylsiloxy-1,3,2-dioxaphospholans with benzil.[39] Silylated spiro-phosphoranes are formed at a low temperature (between −40 °C and −50 °C) and on heating are fully transformed into the corresponding cyclic phosphates:



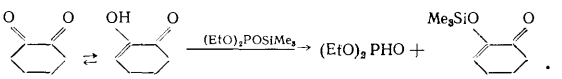
A product with a phosphate structure has also been isolated in the reaction of silyl phosphites with benzoylformic acid ester:[30]



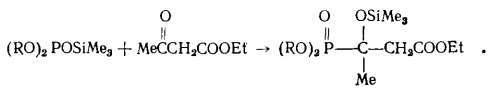
Both pathways leading to stabilisation, namely the migration of the Me_3Si group and the phosphonate–phosphate rearrangement, are realised in the reaction with the nitrile of benzoylformic acid:[30]



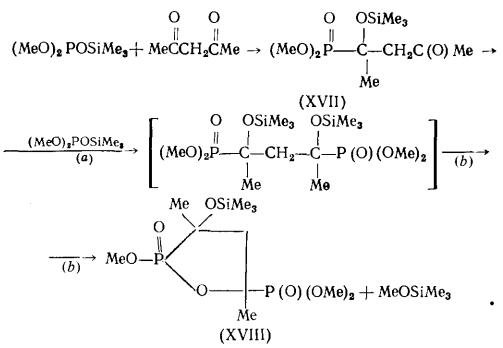
The attempt to obtain the products of the addition of diethyl trimethylsilyl phosphite to cyclohexane-1,2-dione was unsuccessful. The reaction results in the quantitative formation of diethylphosphorous acid and 2-trimethylsiloxycyclohexenone, i.e. the diketone reacts in the enolic form:[40]



The involvement of the enolic form also in the reaction of silyl phosphites with acetoacetic ester might have been expected, but in this case the product of addition to the C=O group is formed exclusively:[5,41]

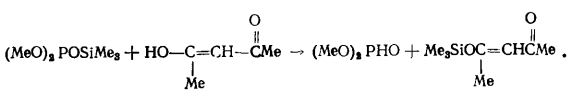


The reaction of acetylacetone resulted in the isolation of 5-dialkylphosphoryl-1,2-oxaphospholan (XVIII) together with α-siloxyphosphonate (XVII):[41]

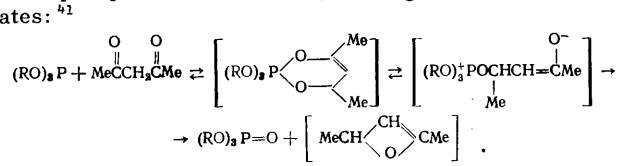


The preferential formation of only one diastereoisomer of 1,2-oxaphospholan (XVIII) has been explained[41] by the stereospecificity of the attack by silyl phosphite on the carbonyl group of the 1:1 adduct [stage (*a*)] and also by the stereospecificity of the cyclisation reaction (*b*), because there are three bulky groups at the interacting atoms in the transition state: two dialkylphosphoryl groups and one trimethylsilyl group.

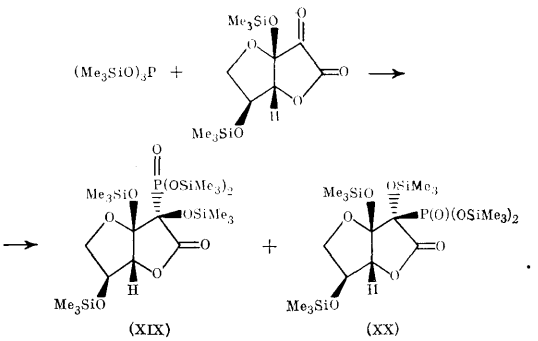
Another reaction pathway, namely the silylation of the enol of acetylacetone, has also been noted:



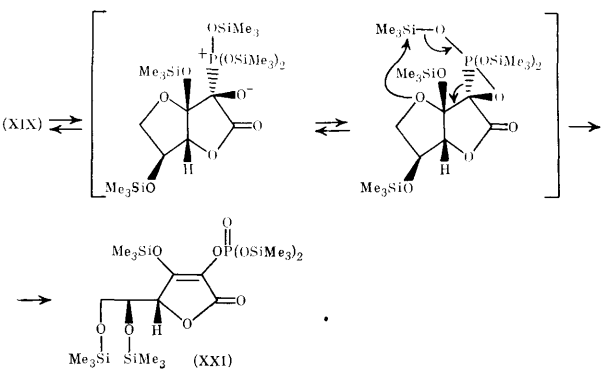
In contrast to silyl phosphites, trialkyl phosphites react with acetylacetone and acetoacetic ester via the intermediate phosphorane structures, forming trialkyl phosphates:[41]



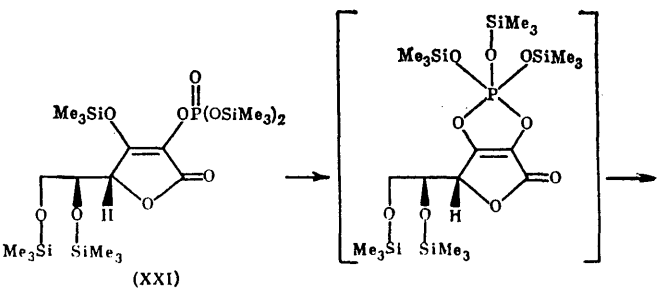
The conformational characteristics of bicyclic α-ketolactones are responsible for the possibility of the formation of the diastereoisomeric phosphorates (XIX) and (XX) as a result of the nucleophilic attack by silyl phosphite on the carbonyl carbon atom from different sides of the plane of the lactone ring:[42]

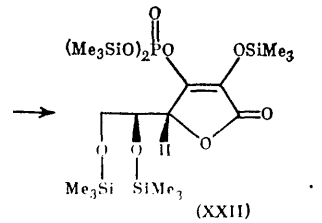


The adducts (XIX) and (XX) isomerise to the 2-*O*-phosphate (XXI) on heating. The diastereoisomer (XIX), which is a product of the attack by silyl phosphite on the carbonyl group from the rear of the plane of the ring, then undergoes a thermal rearrangement at a higher rate than the isomer (XX), which is caused by favourable conditions for the formation of a six-membered cyclic transition state:



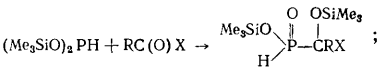
The transformation of the phosphonate (XX) into the 2-*O*-phosphate (XXI) evidently includes the decomposition of compound (XX) into the initial compounds and subsequent formation of the diastereoisomer (XIX), whose pyrolysis leads to the phosphate (XXI). The 2-*O*-phosphate (XXI) also isomerises to the 3-*O*-phosphate (XXII) via the intramolecular migration of the phosphoryl group during the thermal rearrangement:





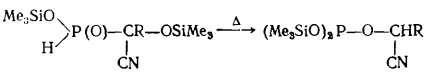
(XXII)

Bis(trimethylsilyl) hypophosphites add to the carbonyl group in ketophosphonates, ketonitriles, and acetoacetic ester with retention of the P–H bond: [29]

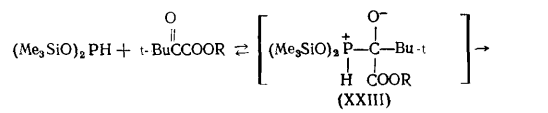


R=Me, t-Bu; X=P(O)(OEt)$_2$, CN, CH_2COOMe .

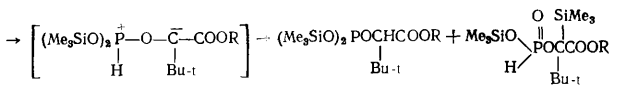
The products formed in this process are thermally unstable and decompose into a series of compounds on heating. α-Cyanoalkyl bis(trimethylsilyl) phosphites are formed from trimethylsilyl α-cyano-α-trimethylsiloxyalkylphosphonites: [29]



Increasing steric hindrance of the carbonyl carbon atom in trimethylpyruvic acid esters, combined with the electron-accepting influence of the alkoxycarbonyl group, promotes the rearrangement of the intermediate dipolar ion (XXIII) with a P–C bond to the ion (XXIV) with a P–O–C bond. The intermediate is then stabilised via the migration of a proton or Me_3Si group to the carbanionic centre: [29]

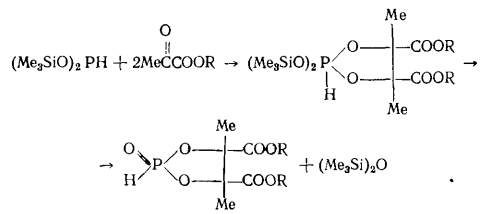


(XXIII)



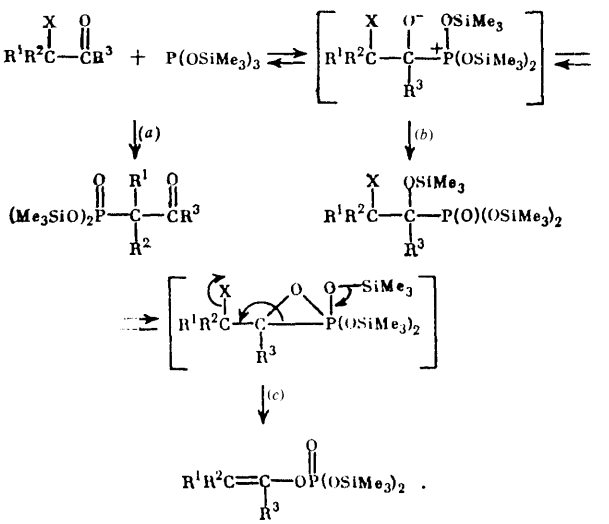
(XXIV)

The interaction of silyl hypophosphite with pyruvic acid esters leads to 4,5-dialkoxycarbonyl-2-hydro-4,5-dimethyl-2,2-bis(trimethylsiloxy)-1,3,2-dioxaphospholans with a pentacoordinate phosphorus atom, which are slowly converted into 4,5-dialkoxycarbonyl-2-hydro-4,5-dimethyl-2-oxo-1,3,2-dioxaphospholans: [29]



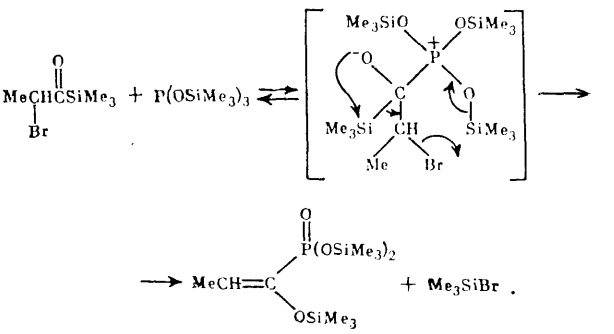
3. Interaction with Halogen-Containing Carbonyl Compounds

The reactions of trialkyl phosphites with α-halogeno-substituted carbonyl compounds result in the formation of either the enol phosphate esters (the Perkow reaction) or of 2-oxophosphonates (the Arbuzov reaction). [12] The ratio of the products depends on the structure of the carbonyl compound and the experimental conditions. A different pathway is characteristic of organosilicon derivatives of tervalent phosphorus in their reactions with α-halogeno-substituted aldehydes and ketones, namely addition to the C=O group with formation of α-trimethylsiloxyalkylphosphonates [pathway (*b*)]. [43,44] At the same time the products of the Arbuzov reaction [pathway (*a*)] and the Perkow reaction [pathway (*c*)] have been isolated in the reactions involving phenacyl halides, α-halogenoacetates, and esters of α-halogenopyruvic acid: [36,43,44]



A general reaction mechanism has been proposed, [43] including the initial formation of a dipolar intermediate and a subsequent rapid intramolecular transfer of the Me_3Si group to the *O*-anionic centre. Electron-accepting substituents (Ph, COOR) at the C=O group promote the phosphonate–phosphate rearrangement and the formation of the products of the Perkow reaction. The electron-donating alkoxy-group in α-halogenoacetates suppresses the addition of silyl phosphites to the carbonyl group—only the direct substitution of the halogen with the formation of alkoxycarbonylalkylphosphonates (the Arbuzov reaction) takes place.

An interesting result has been obtained in the reaction of α-bromoethyl trimethylsilyl ketone with tris(trimethylsilyl) phosphite. [44] The rapid 1,2-migration of the trimethylsilyl group to the negatively charged oxygen atom of the dipolar intermediate (XXV) overtakes the 1,4-silylotropic transition and the phosphonate–phosphate rearrangement. The subsequent β-elimination of the bromide ion leads to a mixture of the *Z*- and *E*-phosphonates (XXVI):



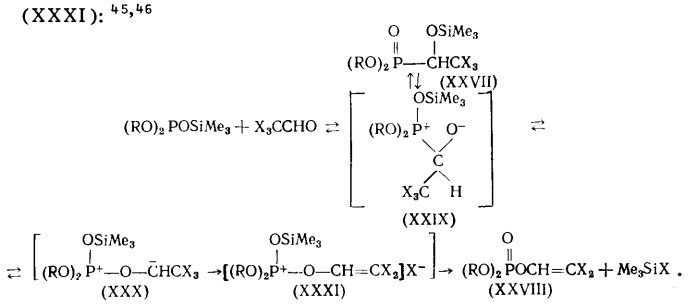
Z-, *E*-(XXVI)

A characteristic feature of the chemical behaviour of silyl phosphites in reactions with various carbonyl compounds, including α-halogeno-derivatives, is their capacity to add readily to the C=O group. As shown above, this constitutes a significant difference between silyl phosphites and trialkyl phosphites. One of the causes of such reactivity of silyl phosphites in carbonyl addition reactions is the possibility of formation of a five-membered cyclic transition state in the stage involving the transfer of the trimethylsilyl group to the *O*-anionic centre of the dipolar intermediate with formation of α-trimethylsiloxyalkylphosphonates. At the same time, according to Sekine et al.,[44] the electron-donating properties of the Me_3SiO substituent, which are more pronounced than those of the RO groups, may play an important role in this reaction pathway. The electron-donating effect promotes the stabilisation of the phosphonium centre of the intermediate and hinders the phosphonate–phosphate rearrangement. The successive introduction of trimethylsilyl groups into the phosphite molecule alters the reaction pathway: carbonyl addition becomes dominant even in the case of ethyl bis(trimethylsilyl) phosphite.[44] The tendency towards the addition to the carbonyl group of chloroacetone is more marked than in the reaction with bromoacetone (Table 2).

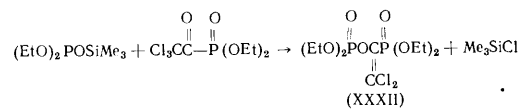
Table 2. The relative ease of various pathways in the interaction of phosphorus(III) derivatives with halogenoacetones (Ad = addition to the carbonyl group, A = Arbuzov reaction, P = Perkow reaction[44]).

$XCH_2C(O)Me$	$(EtO)_3P$	$(EtO)_2POSiMe_3$	$EtOP(OSiMe_3)_2$	$P(OSiMe_3)_3$
X=Cl	A< P	Ad	Ad	Ad
X=Br	A∼P	A< P	Ad	Ad

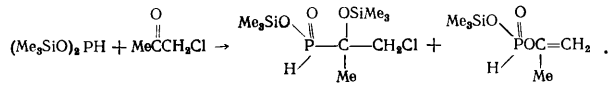
In those cases where there is a possibility of the formation of α-siloxyphosphonates and vinyl phosphates, the addition to the carbonyl group is the kinetically controlled process and the Perkow reaction takes place under the conditions of thermodynamic control. Thus the interaction of silyl phosphites with trihalogenoacetaldehyde leads initially to the formation of the phosphonates (XXVII), which decompose on prolonged heating into vinyl phosphates and a halogenosilane via a pathway involving the formation of the zwitter-ionic intermediates (XXIX) to (XXXI):[45,46]



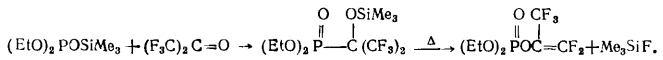
The reaction of diethyl trimethylsilyl phosphite with trichloroacetylphosphonate takes place via an analogous mechanism and leads to the unsaturated phosphoryloxyphosphonate (XXXII):[47]



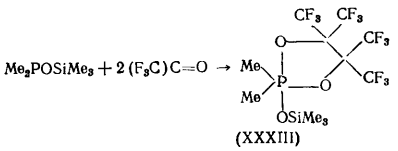
Bis(trimethylsilyl) hypophosphite reacts with chloroacetone to form α-siloxyphosphonate and vinyl phosphate:[29,48]



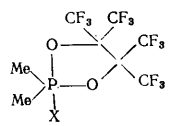
Various reaction pathways have been noted also for the reactions of diethyl trimethylsilyl phosphite and trimethylsilyl dimethylphosphinite with hexafluoroacetone. In the former case the authors[15] detected the formation of the intermediate diethyl hexafluoro-α-trimethylsiloxypropylphosphonate, which is converted into vinyl phosphate at a high temperature (160 °C) in 3 h:



Trimethylsilyl dimethylphosphinite reacts with two moles of hexafluoroacetone even at −78 °C with the quantitative formation of the thermally highly stable λ^5-1,3,2-dioxaphospholan (XXXIII):[49]

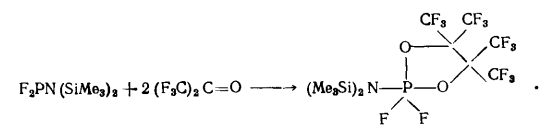


The presence of the mobile Me_3SiO group in compound (XXXIII) makes it possible to synthesise readily a number of derivatives of pentacoordinate phosphorus:

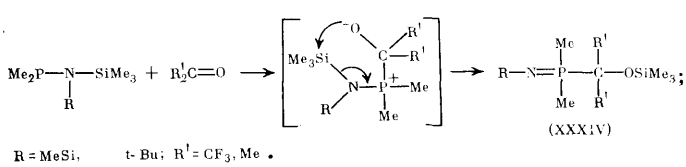


X=F, Cl, NMe_2, N_3, MeO .

Bis(trimethylsilyl)aminodifluorophosphine reacts similarly with hexafluoroacetone:[50]



However, on passing to *N*-alkyl-*N*-silylaminodialkylphosphines, the process develops differently. Nucleophilic attack by the phosphorus atom of the aminophosphine on the carbonyl carbon atom is accompanied by the 1,4-transfer of the Me_3Si group from nitrogen to oxygen and leads to the adduct (XXXIV) having the imino-structure:[51]

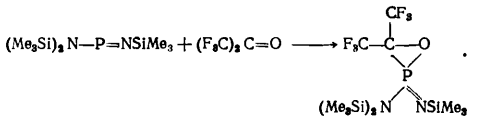


R = MeSi, t-Bu; R' = CF_3, Me .

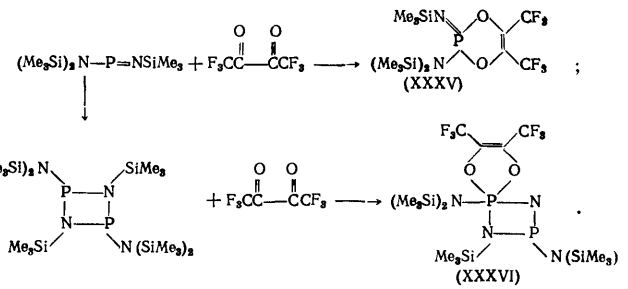
Thus the variation of the nucleophilic properties of the phosphorus(III) centre combined with the high lability of the Si–N bond in silylaminophosphines is reflected significantly in the character of the interaction with carbonyl

reagents, permitting the synthesis of various types of organophosphorus compounds with functional group substituents.

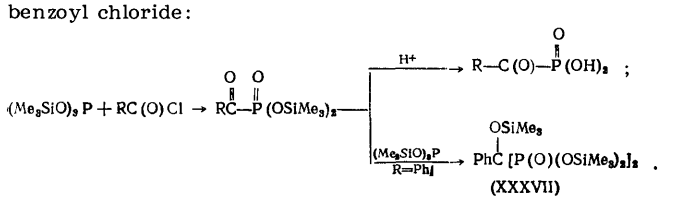
The reaction of the *N*-silylated amide of phosphenimidous acid with hexafluoroacetone is unusual. The [1 + 2]-cycloaddition yielded a new three-membered cyclic adduct, namely 2-[bis(trimethylsilyl)amino]-3,3-bis(trifluoromethyl)-2-trimethylsilylimino-1,2-λ^5-oxaphosphiran: [52]



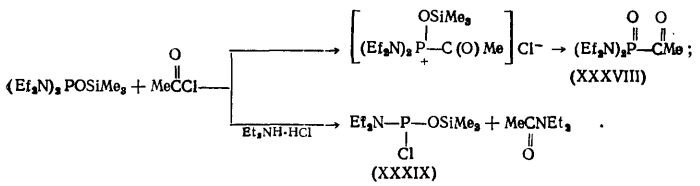
The reactions of the phosphenimidous amide and its dimer with hexafluorodiacetyl lead to the [1 + 4]-cycloaddition products (XXV) and (XXXVI) respectively: [52]



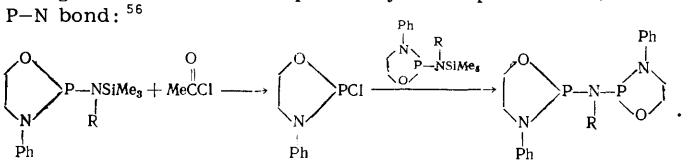
Like trialkyl phosphites, silyl phosphites give rise to the corresponding acylphosphonates on interaction with acyl halides. [53,54] The use of tris(trimethylsilyl) phosphite in this reaction makes it possible to synthesise readily the free acylphosphonic acids; the silylated α-hydroxybenzyldiphosphonate (XXXVII) can be obtained by reaction with benzoyl chloride:



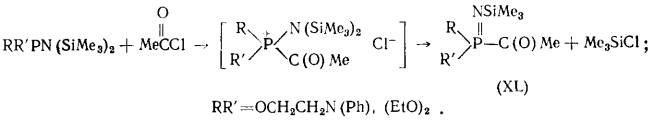
Trimethylsilyl *N,N,N',N'*-tetra-alkylphosphorodiamidites react with acetyl chloride to form the Arbuzov reaction products (XXXVIII) and the products (XXXIX) resulting from the substitution of the amino-group: [55]



The interaction of monosilylated 2-amino-1,3,2-oxazaphospholans with acetyl chloride proceeds with involvement of the nitrogen atom and is accompanied by the rupture of the P–N bond: [56]



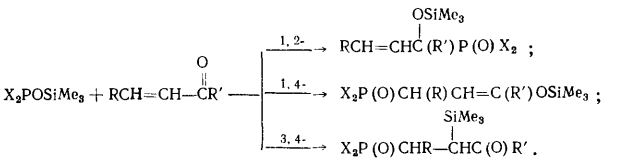
The introduction of a second Me_3Si group results in a change of the reaction centre—*N*-trimethylsilylacetylphosphonimidates (XL) are formed in the reaction: [56]



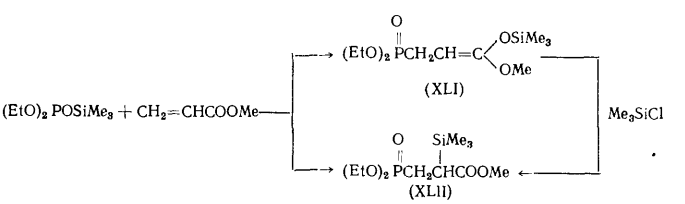
Thus the character of the interaction of the organosilicon derivatives of tervalent phosphorus with halogenocarbonyl compounds depends on the nature of the substituents in the reactant. In most cases the reactions apparently proceed via a nucleophilic mechanism; a dipolar ion with a P–C bond is formed initially and can be stabilised in different ways: (1) by the 1,4-transfer of the Me_3Si group to the oxygen ion with formation of α-siloxyphosphonates; (2) by the Perkow reaction with elimination of a halogenosilane; (3) by the addition of a second molecule of the carbonyl compound and the formation of 1,3,2-dioxaphospholans. Other reaction pathways are also possible, particularly those involving organosilicon reagents containing the P(III)–N–Si fragment.

4. Reactions with αβ-Unsaturated Carbonyl Compounds

The reactions involving addition to unsaturated carbonyl compounds occupy an important place in the chemistry of phosphorus–silicon compounds containing the P(III)–X–Si (X = O or N) group. The possibility of the involvement of the carbonyl and vinyl centres of the unsaturated reactant in these processes determines the simultaneous occurrence of three competing reactions: addition to the 1,2-, 3,4-, and 1,4-positions of the enone; their ratios are determined by the nature of the substituents in the initial compounds:

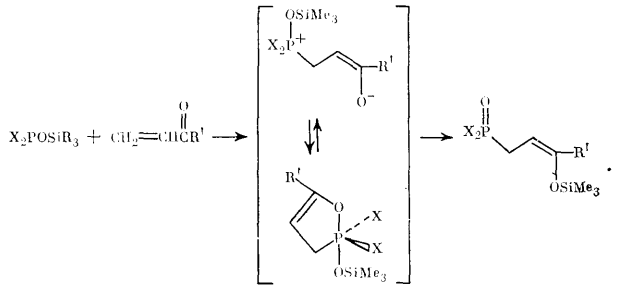


Dialkyl trimethylsilyl phosphites react vigorously with unsaturated aldehydes via the 1,2- and 1,4-addition pathways in the absence of catalysts, [5,10,11,18–20] while silyl phosphoramidites form exclusively the 1,2-adducts. [11] The interaction of trialkylsilyl phosphites and trialkylsilyl phosphoramidites with vinyl ketones takes place under more severe conditions and is accompanied by the preferential formation of 1,4-adducts. [10,11,19,57] The introduction of electron-donating alkoxy-substituents at the carbonyl centre (esters of αβ-unsaturated carboxylic acids) renders only the 1,4- and 3,4-addition reactions energetically favourable. [4,5,58] The phosphorylated derivatives of alkyltrimethylsilylketen acetals (XLI) rearrange to the *C*-silylated phosphonates (XLII) on treatment with halogenosilanes: [7]



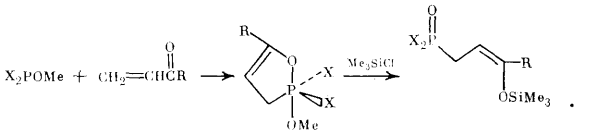
The study of the stereochemical characteristics of the reactions of silyl phosphites with unsaturated carbonyl compounds and the elucidation of the factors determining

the composition of the reaction products resulted in two pathways leading to the formation of 1,2- and 1,4-adducts being proposed.[19] The first is analogous to the mechanism of the addition of silyl phosphites to the carbonyl groups of unsaturated aldehydes and ketones examined above. The mechanism of the 1,4-addition is presented below:



(XLIIIa)

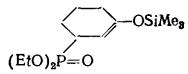
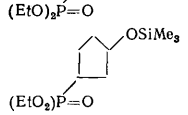
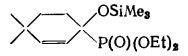
The preferential formation of the *Z*-adduct as well as the absence of the interaction of the silyl phosphite with an equimolar amount of cyclohexene (100 °C, 52 h) shows that the cisoid geometry of the enone promotes the 1,4-addition. It is believed that[19] the intermediate formation of the oxaphospholen (XLIIIa) in this reaction is probable, because the silylation of the methoxy-analogues (XLIIIb) also results in phosphorylated *Z*-silylenols:



(XLIIIb)

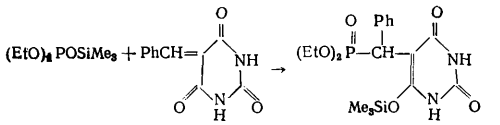
The independent occurrence of the 1,2- and 1,4-addition reactions is confirmed by the finding that the corresponding adducts are thermally stable and do not isomerise to one another (200 °C, 24 h).[19] The low sensitivity of the ratio of the 1,2- and 1,4-adducts to changes in the solvating properties of the medium indicates only a small charge separation in the transition states of the rate-determining stages of both addition reactions.

Table 3. Reactions of cyclic enones with $(EtO)_2POSiMe_3$.[60]

Initial enone	Main product	*T*, °C	τ, h	α
		80 180	75 12	8:1 16:1
		80 180	12 12	100:1 100:1
		80 180	200 18	1:3 1:19

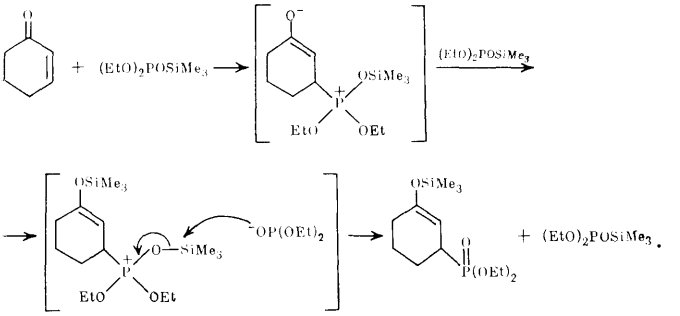
Notation: *T* is the reaction temperature, τ the reaction time, and α the ratio of the 1,4- and 1,2-adducts.

The reaction of diethyl trimethylsilyl phosphite with 5-benzylidenebarbituric acid apparently also proceeds by the 1,4-shift mechanism:[59]



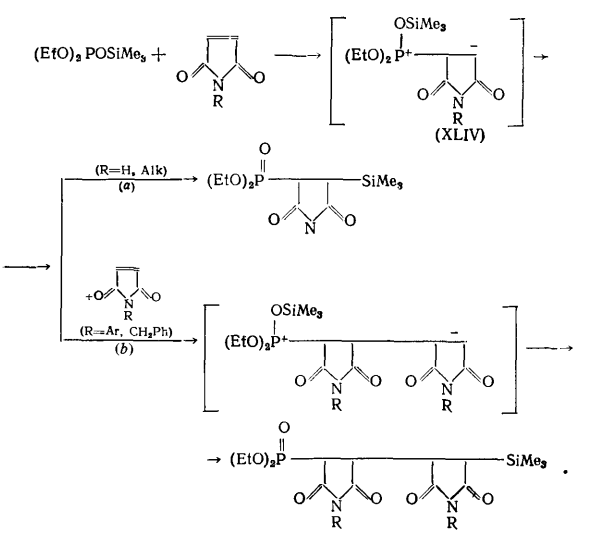
The rigid fixation of the *s-trans*-conformation of the unsaturated carbonyl compound alters the mechanism of the addition reaction. Cyclic enones form stable 1,4- and 1,2-adducts with diethyl trimethylsilyl phosphite only after prolonged heating of the reactants.[60] The ratio of the 1,4- and 1,2-adducts depends significantly on the experimental temperature and on the steric accessibility of the β-carbon atom of the unsaturated cyclic ketone (Table 3).

The mechanism of the formation of 1,4-adducts from cyclic enones presupposes the intermolecular transfer of the Me_3Si group with participation of a second silyl phosphite molecule:



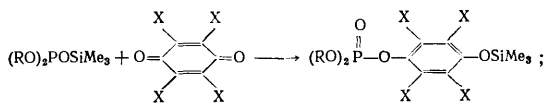
The appreciable acceleration of the reaction in the presence of an excess of silyl phosphite and the high sensitivity to changes in the dielectric properties of the medium (the reaction with $CHCl_3$ is much slower than that with MeCN), which confirms the formation of intermediate dipolar structures, are evidence in support of the mechanism proposed by the authors.[60]

The stabilisation of the intermediate (XLIV) in the reactions of silyl phosphites with maleimides, which also have the *s-trans*-configuration of the C=C and C=O bonds, can be achieved in different ways depending on the nature of the substituents R at the nitrogen atom:[61,62]



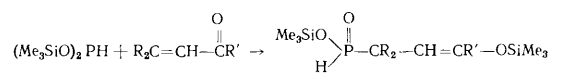
In order to elucidate the causes of the different types of chemical behaviour of *N*-substituted maleimides, measurements were made of the half-wave potentials of the polarographic reduction of these substances.[61] The values of $E_{\frac{1}{2}}$ for compounds with R = Ph, CH_2Ph, or p-ClC_6H_4, determined in dimethylformamide (DMF), proved to be greater than the corresponding values for the imides with R = H or Bu, which indicates more pronounced electrophilic properties of the *N*-aryl and *N*-benzyl structures. Maleimides containing electron-accepting substituents readily add to the carbanionic centre of the intermediate zwitter-ion (XLIV) [pathway (*b*)] and this reaction is faster than the 1,4-shift of the trimethylsilyl group [pathway (*a*)]. The stabilisation of the intermediate (XLIV) by electron-accepting groups in maleimide, which increases the lifetime of the intermediate compound and thereby favours the intermolecular addition of a second molecule of the unsaturated reactant [pathway (*b*)] plays an important role in the formation of adducts having the 1:2 composition. On the other hand, a decrease of the nucleophilicity of the carbanion in the 1:1 intermediate lowers the rate of the competing silylotropic process.

The interaction of silyl phosphites with p-quinones proceeds differently. The addition is at the 1,6-positions of the quinonoid system and leads to products having the phosphate structure:[34,63]

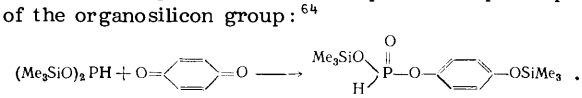


X=H, Cl .

Mainly 1,4-adducts are formed in the reactions of bis(trimethylsilyl) hypophosphite with unsaturated carbonyl compounds by migration of an Me_3Si group to carbonyl oxygen:[29]



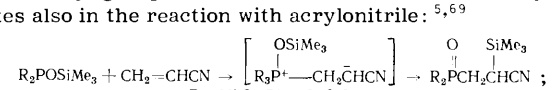
The addition to p-quinones also takes place with participation of the organosilicon group:[64]



The character of the interaction of silyl phosphites with nitro-olefins is in many respects similar to that of reactions involving 1,4-addition to unsaturated carbonyl compounds. The nucleophilic attack by the phosphorus atom on the β-carbon atom of the ethylenic bond results in the formation of the intermediate dipolar ion (XLV), which rapidly isomerises to the silyl ester of the phosphorylated nitronic acid (XLVI).[65,66] In the reaction of 3,3-trichloro-1-nitroprop-1-ene the dipolar intermediate can be stabilised not only by the transfer of the Me_3Si group but also by the prototropic transition (XLV) → (XLVII) with the subsequent elimination of chlorosilane from the unsaturated quasi-phosphonium intermediate (XLVIII).[67]
Trialkyl phosphites under the same conditions form esters of alkylenephosphonic acids and alkyl nitrites.[68]

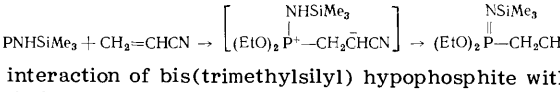
5. Reactions with Other Unsaturated Compounds

Organosilicon derivatives of tervalent phosphorus are capable of reacting with various unsaturated compounds containing the C=C, C=N, C=S, N=O, and S=O bonds and heterocumulene fragments. An example, namely the addition to maleimides, was examined above. The mechanism, involving the initial addition of silyl phosphites to the β-carbon atom of the activated double bond and the subsequent migration of the silyl group to the carbanionic centre, evidently operates also in the reaction with acrylonitrile:[5,69]

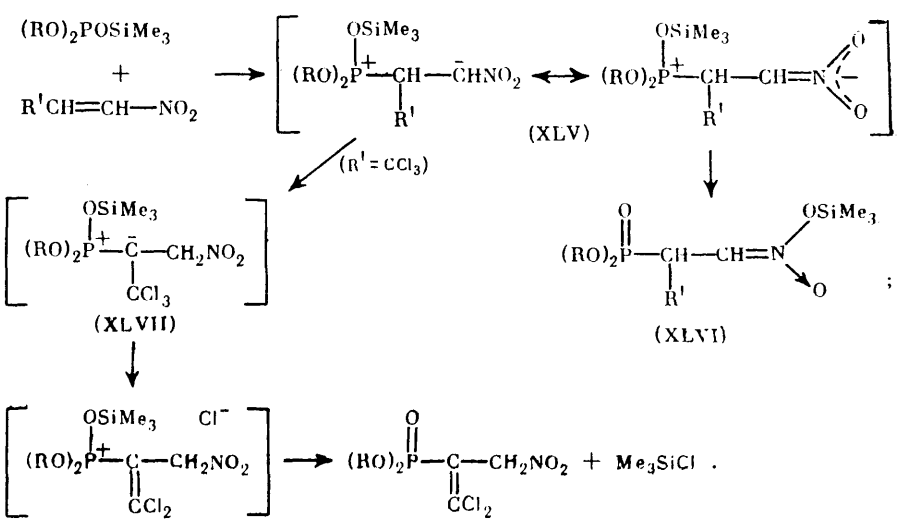


R=AlkO, Ph, Me_3SiO .

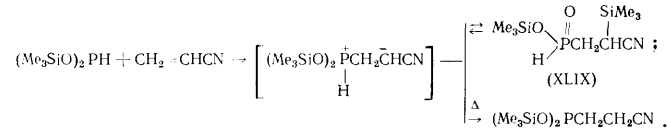
Diethyl *N*-trimethylsilylphosphoramidite also readily reacts with acrylonitrile. As a result of the prototropic transition, diethyl *N*-trimethylsilyl-β-cyanoethylphosphonimidate is formed under these conditions:[70]



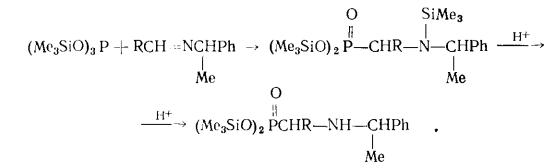
The interaction of bis(trimethylsilyl) hypophosphite with acrylonitrile and styrene leads to substituted bis(trimethylsilyl) ethylphosphonites.[71,72] It has been established by low-temperature ^{31}P NMR [72] that the reaction of the hypophosphite with acrylonitrile involves the initial formation, as a result of the migration of the Me_3Si group, of monosilyl phosphonite (XLIX), which isomerises at a higher



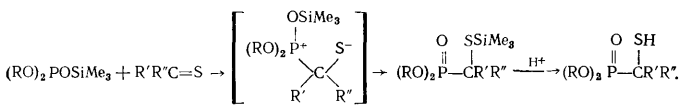
temperature to a thermodynamically controlled product—the disilyl phosphonite (L):



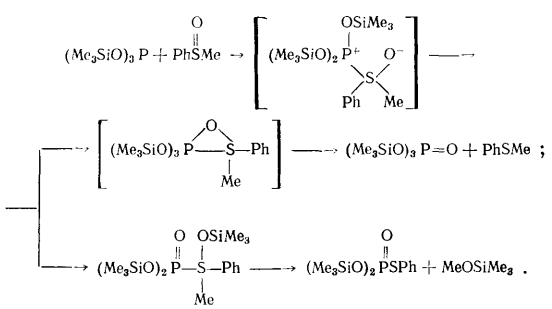
Tris(trimethylsilyl) phosphite is capable of adding to the C=N bond in aldimines: [73]



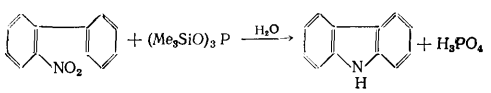
The reactions of silyl phosphites with cyclohexanethione and ethyl methyl thioketone lead readily to the dialkyl esters of α-trimethylsilylthioalkylphosphonic acid: [74]



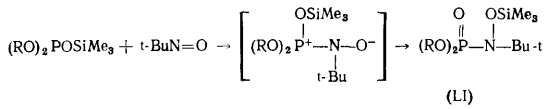
Tris(trimethyl silyl) phosphite exhibits a very high deoxygenating activity in interaction with sulphoxides and nitro-compounds. [75] In the reaction with methyl phenyl sulphoxide the main products are a sulphide and a silyl phosphate. However, the decomposition of the dipolar intermediate arising in the first stage takes place apparently also via the 1,4-migration of the organosilicon group and leads to *S*-phenyl phosphorothioate via a phosphorylated sulphurane:



The deoxygenation of nitro-compounds can lead to nitrogen-containing heterocycles: [75]

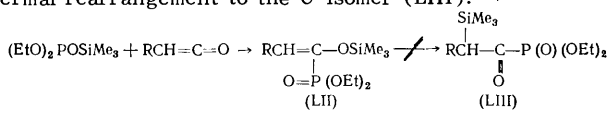


Nitroalkanes react with silyl phosphites like carbonyl compounds: the initial step in the interaction is nucleophilic attack by the phosphorus atom on the nitrogen atom of the nitroso-group; the subsequent 1,4-silylotropic shift leads to stable adducts having the phosphoramidate structure (LI): [76]

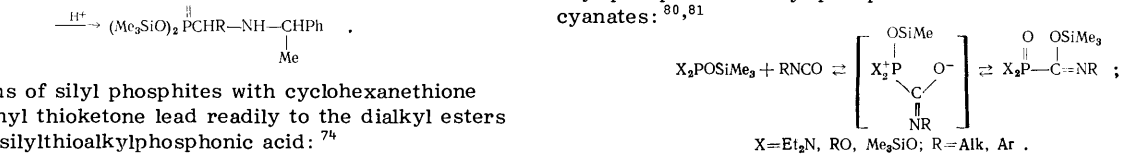


Trialkyl phosphites are oxidised by nitrosoalkanes to phosphates. [77]

A characteristic feature of the interaction of silyl phosphates with heterocumulenes is the possibility of the involvement in the reaction of one or several reaction centres of the unsaturated system. The addition of silyl phosphites to keten leads to the quantitative formation of the *O*-silyl derivative (LII), which does not undergo a thermal rearrangement to the *C*-isomer (LIII): [78,79]



An analogous addition to the carbonyl fragment of a heterocumulene has also been observed in the reactions of silyl phosphites or silyl phosphoramidites with isocyanates: [80,81]

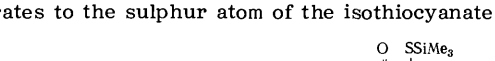


On heating, the reaction products decompose into the initial compounds. The thermal stability of the adducts with phenyl isocyanate is much higher than that of the adducts with the alkyl analogues by virtue of the conjugation of the C=N bond with the aromatic ring. [81]

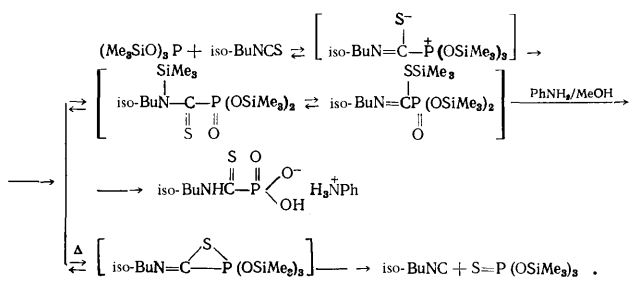
The interaction of phosphorus–silicon reagents with isothiocyanates does not proceed quite so unambiguously. Silyl phosphoramidites readily add to the C=N bond of phenyl isothiocyanate with formation of the amides of *N*-phenyl-*N*-trimethylsilylthiocarbamoylphosphonic acids: [80]



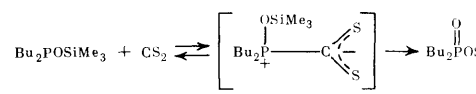
In the case of tris(trimethylsilyl) phosphite the Me_3Si group migrates to the sulphur atom of the isothiocyanate: [81]



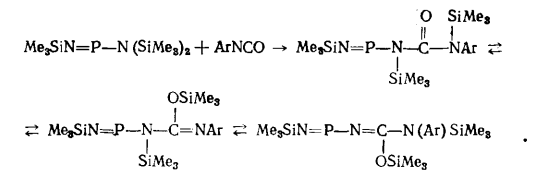
The mode of reaction of silyl phosphite with isobutyl isothiocyanate is determined by the experimental temperature. At room temperature a 1:1 adduct is formed and has been isolated in the form of the monoanilinium salt of *N*-isobutylthiocarbamoylphosphonic acid (LIV). Heating of the reaction mixture at 100 °C is accompanied by the desulphurisation of the isothiocyanate: [81]



The mechanism of the formation of phosphorothioates in this reaction is apparently analogous to the mechanism of the interaction of silyl phosphinites with carbon disulphide: [82]

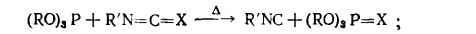


The addition of the *N*-silylated amide of *N*-(trimethylsilyl)phosphenimidous acid to aryl isocyanates leads to an equilibrium mixture of adducts;[83] the phosphorus atom remains dicoordinate under these conditions:

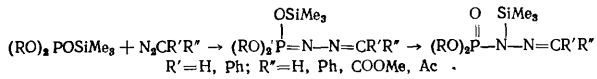


The complexity of the signals due to the Me_3Si group in the ^1H NMR spectrum and its dependence on temperature and the nature of the solvent demonstrate, according to the authors,[83] the occurrence of the amide–imide tautomerism and the 1,3-migration of the silyl group in the N=P–N triad.

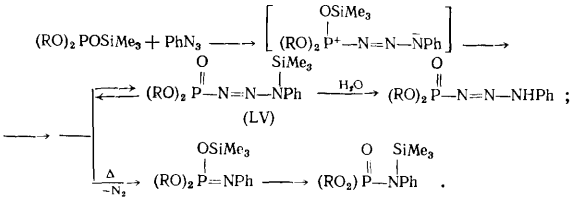
Trialkyl phosphites are known[84] to react with isocyanates and isothiocyanates under severe conditions (150–180 °C) with formation of isonitriles:



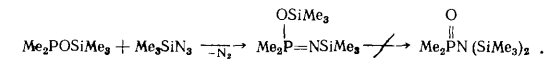
The first stage of the reaction of silyl phosphites with diaza-compounds involves the formation of phosphazenes, which isomerise to phosphorohydrazidates even at room temperature:[85,86]



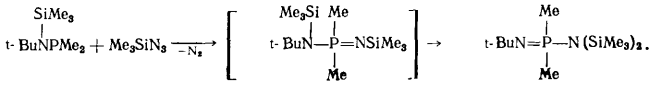
When silyl phosphite reacts with phenyl azide, the kinetically controlled product is 1-dialkylphosphoryl-3-phenyl-3-silyltriazene (LV), which is readily hydrolysed by atmospheric moisture. With increase of temperature, conditions are attained for the irreversible decomposition of the intermediate betaine with evolution of nitrogen and formation of *N*-silylphosphoramidate:[87]



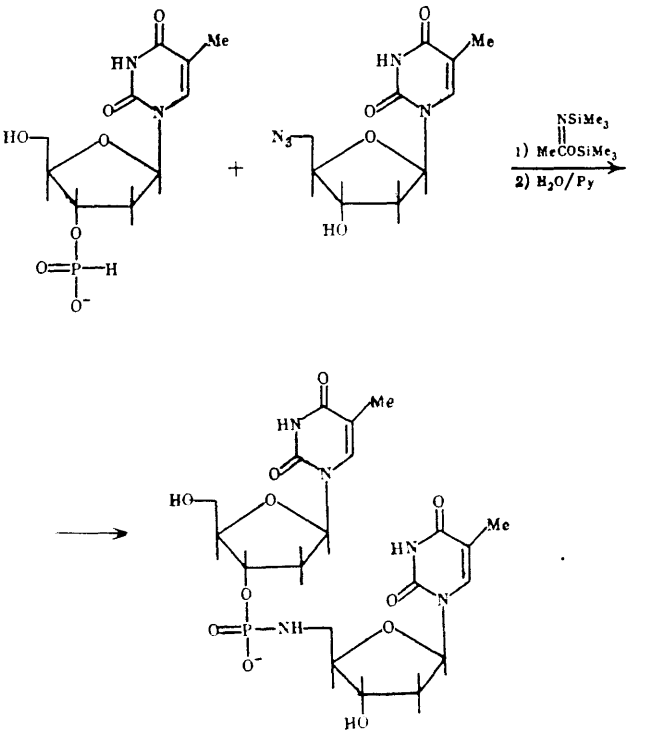
An increase of steric hindrance at the nitrogen atom in the phosphimine prevents the O → N migration of the Me_3Si group:[88,89]



The imination of *N*-t-butyl-*N*-trimethylsilylaminodimethylphosphine with trimethylsilyl azide results in the formation of a phosphimine with the sterically most favourable disposition of the bulky groups:[90]



The silyl phosphite–azide method of synthesis of phosphoramidates can be applied successfully to the synthesis of biologically important compounds:[88]



The data on the reactions involving the addition of organosilicon derivatives of tervalent phosphorus to various unsaturated compounds examined in this Section show that in the majority of the processes, as in the case of systems containing the P–X–C fragment, the initial step of the interaction is attack by the phosphorus(III) atom on the electrophilic centre of the other reactant. Consequently the replacement of the organic substituent in the phosphorus-containing reactant by the trialkylsilylgroup does not have a significant influence on the nucleophilic character of the phosphorus atom.

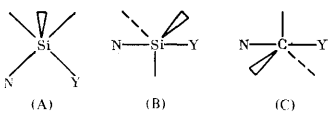
Extensive experimental and theoretical data showing that the overall electronic effect of the R_3Si group consists of the inductive and mesomeric interactions have accumulated in the literature.[91–98] The inductive effect is quantitatively expressed by the σ^* constants.[99] The electron-accepting influence of the R_3Si group [conjugation of the $(p-d)_\pi$, $(\sigma-4s)$, and $(\sigma-3d)_\sigma$ types] depends both on the nature of the heteroatom X in the fragment $\overset{\frown}{Si-X}-R$ and on the competing interaction $\overset{\frown}{X-R}$.[93,100] The replacement of the alkyl substituent at the oxygen or nitrogen atom by the trimethylsilyl group in isotypical compounds leads to a decrease of electron density at the heteroatom. The basicity of silyl ethers and silylamines is lower than that of their carbon analogues.[101–105]

The available literature data concerning comparative estimates of the nucleophilic properties of organosilicon derivatives of tervalent phosphorus are contradictory. Qualitative comparison of the reactivities of trialkyl and silyl phosphites shows, in the view of a number of investigators,[19,106,107] that the introduction of the Me_3SiO substituent at the phosphorus atom increases the nucleophilic reactivity of the phosphorus(III) system. On the other hand, the half-wave potentials $E_{1/2}$ (in volts) of the full esters of phosphorous acids, determined at a platinum electrode in acetonitrile[108,109] [1.60 for $(EtO)_3$; 1.66 for

$(MeO)_3P$; 1.74 for $(EtO)_2POSiMe_3$; 1.78 for $(MeO)_2$. $.POSiMe_3$; 1.96 for $(Me_3SiO)_3P$] indicate the electron-accepting influence of the organosilicon group.

Spectroscopic study of the hydrogen-bonded complexes of dialkyl and bis(trimethylsilyl) phosphites with phenol demonstrated approximately identical basicities of the oxygen atom in the P=O group in the two compounds.[110]

All these factors suggest that the unusual chemical behaviour of systems incorporating the P(III)–X–Si group is determined not only, and even not so much, by the change in electron density at the phosphorus atom as by the specific role of the trialkylsilyl group in stabilising the dipolar intermediates formed. Nucleophilic substitution at the silicon atom requires a low activation energy and can proceed via two transition states of types (A) and (B) having similar energies.[111–113] Depending on the structure of the intermediate compound and the experimental conditions, a particular version of the silylotropic transition obtains:



(A) (B) (C)

In the case of alkyl derivatives of tervalent phosphorus the only possible way in which the nucleophile can approach the sp^3-carbon atom leads to a trigonal bipyramidal structure of the transition state (C) with an axial disposition of the entering (N) and leaving (Y) groups. The distance between the nucleophilic centres should then be 3.5–4.5 Å.[113] All this increases sharply the energy barrier to the intramolecular transfer of the alkyl group and is responsible for the intermolecular reaction mechanism.

The driving force of the Ad† reactions of silyl phosphites with unsaturated compounds is in our view the thermodynamic ease of the formation of the phosphoryl group; for *N*-silylphosphoramidates, both the differences between the energies of the N–P(III) and N–P(IV) bonds and the greater strength of the Si–O bond compared with the Si–N bond play an important role in stabilising the adducts.

III. ORGANOSILICON DERIVATIVES OF TETRACOORDINATE PHOSPHORUS

The reactivity of organosilicon derivatives of tetracoordinate phosphorus has been studied to a much lesser extent than that of the corresponding phosphorus(III) compounds. It is known that the systems containing the P(IV)–X–Si (X = O, N, or S) group are capable of splitting off the trialkylsilyl group readily on treatment with proton-donating reagents,[1,114] acid halides,[115] and certain metal salts.[114] The reactions of silyl phosphates and their thio- and seleno-analogues with iodotrimethylsilane have been surveyed in a review.[116] There are no literature data concerning the addition of silyl phosphates or *N*-silylphosphoramidates to unsaturated compounds but the Ad processes involving *S*-trimethylsilyl phosphorodithioates have been studied in fair detail. The cause of this situation will be discussed below.

†Addition to carbonyl group—see Table 2 (Ed.of Translation).

We have analysed the reactivity of *S*-trimethylsilyl phosphorodithioates in addition reactions in comparison with phosphorodithioic acids, because *S*-organyl phosphorodithioates do not enter into Ad reactions. Such comparison of the chemical reactivities of phosphorodithioates containing the S–Si and S–H bonds makes it possible to elucidate clearly the specific features of the reactions of silicon-containing phosphorus systems.

1. Interaction with Carbonyl Compounds and Nitro-Compounds

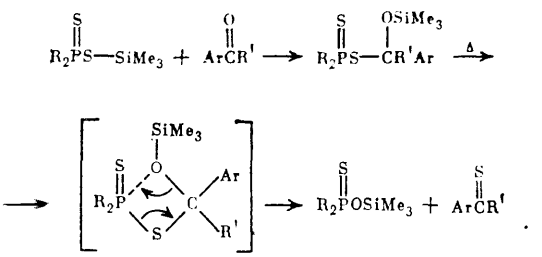
S-Trimethylsilyl esters of phosphorodithioic acids readily add to aliphatic aldehydes in the absence of a catalyst with formation of *S*-(α-trimethylsiloxy)-alkyl ethers:[117]

$$R_2P(S)S—SiMe_3 + R'CHO \rightarrow R_2P(S)S—CHR'—OSiMe_3;$$
R=AlkO, Alk, Ar; R' Alk .

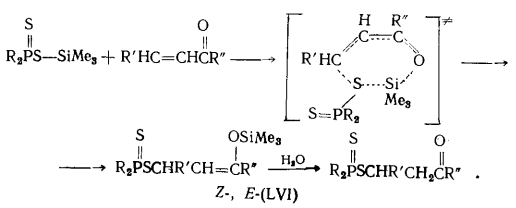
Under analogous conditions, phosphorodithioic acids form bis(dialkylphosphinodithioyl)alkanes:[118]

$$2R_2P(S)SH + R'CHO \rightarrow [R_2P(S)S]_2CHR' .$$

The adducts of silyl phosphorodithioates with aromatic aldehydes and ketones are unstable and decompose on heating via an O,S-exchange process,[117] noted previously for phosphorodithioic acids:[119]



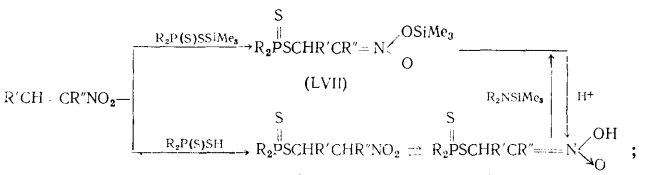
Unsaturated aldehydes and ketones combine vigorously with silyl phosphorodithioates with formation of a mixture of *Z*- and *E*-isomers of phosphorylated silylenols (LVI).[120] The hydrolysis of the adducts leads to 3-oxoalkyl phosphorodithioates obtained from the corresponding phosphorodithioic acids:



Z-, *E*-(LVI)

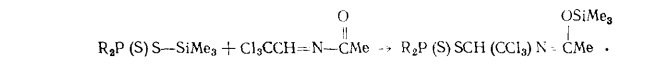
The appreciable, and in the case of acrolein preferential, formation of the *Z*-isomers can be due to the cyclic character of the transition state in the reaction. A similar structure of the activated complex has been proposed for the analogous reactions of phosphorodithioic acids.[121]

The interaction of silyl phosphorodithioates with nitroolefins leads to the formation of 1,4-adducts (LVII, a and b); the hydrolysis of the adduct (LVIIa) gives rise to a mixture of isomers—the nitro-compound (LVIIIa) and the *aci*-nitro-compound (LIXa):[117]



(a) R=MeO, R′=Ph, R″=Me; (b) R=MeO, R′=CCl_3, R″=H.

The silyl esters of phosphorodithioic acids do not add to acrylonitrile, alkyl acrylates, vinyl sulphones, alkyl vinyl ethers, and benzylideneaniline, while phosphorodithioic acids readily form 1,2-adducts with these compounds.[121,122] At the same time silyl phosphorodithioates react vigorously with *N*-acetyltrichloroaldimine:[117]



Thus silyl phosphorodithioates and phosphorodithioic acids show many features in common in their interaction with aromatic aldehydes and ketones but differ in their reactions with aliphatic aldehydes. Comparison of the ways in which the phosphorodithioates react with unsaturated carbonyl compounds and nitro-compounds suggests that the phosphorus-containing addend adds to the terminal positions of the unsaturated system. In the case of silyl phosphorodithioates the 1,4-adducts formed are thermodynamically stable. The addition of phosphorodithioic acids is in most cases accompanied by prototropic isomerisation.[121]

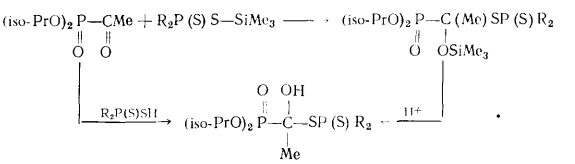
The fact that, in contrast to systems with a P(III)–X–Si group, silyl phosphorodithioates do not add to the C=C bond in unsaturated carbonyl reagents is apparently associated with the necessity for the 1,4-orientation of the silicon-containing phosphorodithioates in the course of the interaction. The driving force of such orientation is the high energy of the Si–O bond (89.3 kcal mol^{-1}) compared with the Si–C (69.3 kcal mol^{-1}) and Si–S (60.9 kcal mol^{-1}) bonds.[123] The coordination of the silicon and oxygen atoms in the transition state also promotes an increase of the nucleophilicity of the sulphur atom of the phosphorodithioate fragment. All these features significantly lower the activation energy for the Ad process.

The reactions of silyl phosphites begin with the nucleophilic attack by the phosphorus atom on the sp^2-carbon atom of the ethylenic bond of the unsaturated reactant.[107] The migration of the Me_3Si group to the basic centre of the intermediate takes place in the second stage of the reaction. The factor determining the reactivity of silyl phosphites is the thermodynamic ease of formation of the P=O bond.

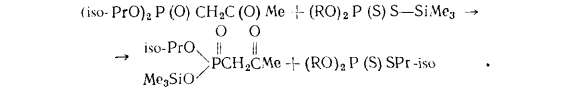
Hence it is clear why phosphorus–silicon reactants containing the P(IV)–O–Si group are incapable, in contrast to silyl phosphites, of adding to various unsaturated systems, including carbonyl systems. This applies to a large extent also to *N*-silylphosphoramidates, although in this instance the deliberate search for suitable reagents may lead to the occurrence of the Ad interaction.

2. Reactions with Organophosphorus Compounds Containing the C=O Group

The mode of reaction of silyl phosphorodithioates with phosphorus-containing carbonyl compounds depends significantly on the structure of the latter. Di-isopropyl acetylphosphonate combines with silyl phosphorodithioates via the carbonyl group, forming siloxy-derivatives. The hydrolysis of the adducts lead to phosphorylated carbinols, also obtained by specific synthesis—by the reaction of phosphorodithioic acid with α-ketophosphonates:[124]

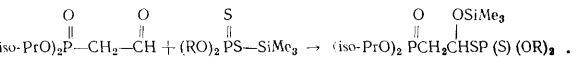


Under these conditions, *O*,*O*-di-isopropylphosphorylacetone undergoes dealkylation:

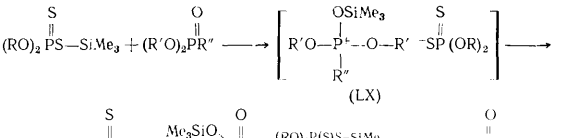


When an excess of silyl phosphorodithioate is used and when methoxy- or ethoxy-groups are introduced at the phosphorus atom of phosphorylacetone, complete silylation of the phosphonate is observed.[124]

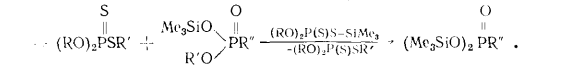
It is noteworthy that *O*,*O*-di-isopropylphosphorylacetaldehyde, which is alkylated with greater difficulty and contains a more reactive carbonyl group, reacts with silyl phosphorodithioates to form adducts via the C=O group:[124]



The dealkylation of phosphonates by silyl phosphorodithioates is a common feature:[124]

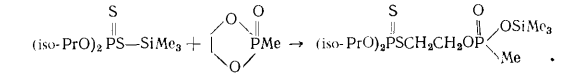


(LX)

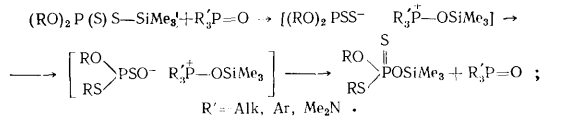


Initially the Me_3Si group of the phosphorodithioate migrates to the phosphoryl oxygen atom with formation of the intermediate quasi-phosphonium compound (LX). The phosphorodithioate anion attacks next the alkyl group of the phosphonium ion, forming the corresponding *S*-alkyl ester of the phosphorodithioic acid and alkyl trimethylsilyl phosphonate. In the case of dimethyl and diethyl phosphonates and in the presence of an excess of silyl phosphorodithioate the dealkylation reaction develops further.

The use of cyclic phosphonates in this reaction makes it possible to synthesise readily compounds with two phosphorus atoms:[124]

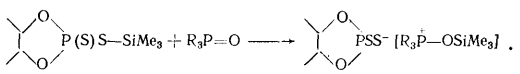


The reaction of silyl phosphorodithioates with organophosphorus systems in which the dealkylation process is impossible (phosphines, phosphine oxides, and hexamethylphosphoramide) does not stop at the stage involving the formation of quasi-phosphonium structures: the isomerisation of the phosphorodithioate anion and subsequent silylation result in the formation of *O*-alkyl *O*-trimethylsilyl *S*-alkyl phosphorodithioates:[124]



R′ = Alk, Ar, Me_2N.

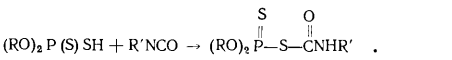
Stable quasi-phosphonium compounds have been isolated in the reaction of a cyclic *S*-silyl phosphorodithioate with phosphine oxides and hexamethylphosphoramide (HMP):



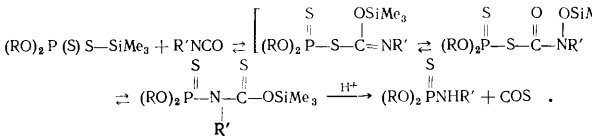
Phosphorodithioic acids react with phosphoryl compounds to form hydrogen-bonded complexes.[125]

3. Reactions with Heterocumulenes

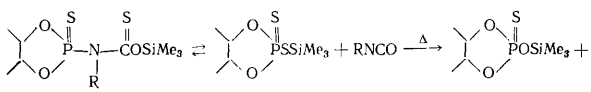
It is known that phosphorodithioic acids add vigorously to the C=N bond in isocyanates to form *N*-organylcarbamoyl phosphorodithioates:[122]



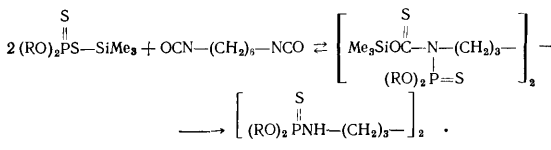
The reactions of silyl phosphorodithioates with various isocyanates have been widely investigated.[126] In the reactions with alkyl isocyanates the products of addition to the N=C=O group of the heterocumulene are formed initially and then rearrange to *N*-thiophosphorylated thiocarbamates via the intermolecular S → N migration of the thiophosphoryl group. The adducts are stable under the usual conditions, but on vacuum fractionation they decompose into the starting materials. This demonstrates the reversibility of the addition reaction and of the phosphorodithioate—phosphoramidothioate rearrangement. The hydrolysis of the reaction product leads to phosphoramidothioates and carbon oxide sulphide:[126]



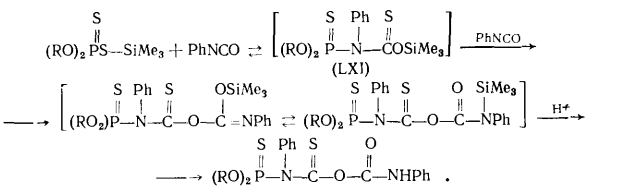
In the reactions involving cyclic silyl phosphorodithioates the products are *N*-thiophosphorylthiocarbamates, which are stable at room temperature, but on heating the O,S-exchange process takes place:



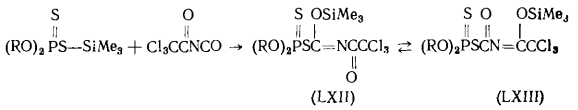
The reactions of the silyl esters of phosphorodithioic acids with hexamethylene di-isocyanate can proceed, depending on the reactant ratio, with participation of one or both isocyanate groups:[126]



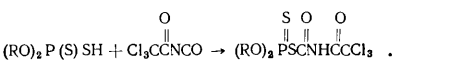
The replacement of the alkyl group in the isocyanate by the phenyl group reduces the reactivity of the heterocumulene—the reaction proceeds at a higher temperature. Two phenyl isocyanate molecules are then involved in the process: the electronic effect of the aromatic ring promotes the nucleophilic addition of the intermediate (LXI) to a second molecule of the unsaturated reactant:[126]



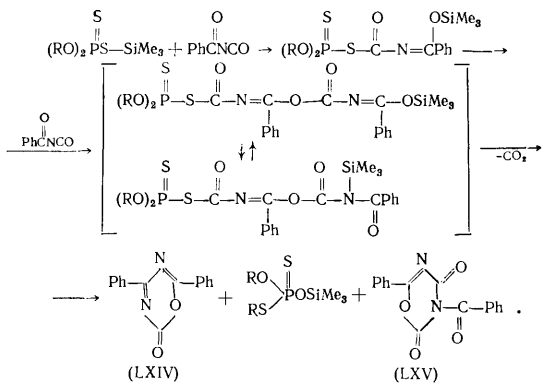
Trichloroacetyl isocyanate readily combines with silyl phosphorodithioates to form the (LXII) ⇌ (LXIII) equilibrium mixture, whose existence is associated with the reversible 1,5-migration of the trimethylsilyl group:



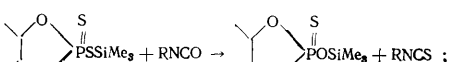
The reaction with phosphorodithioic acids leads to the product of addition to the C=N bond:[126]



In the interaction of silyl phosphorodithioates with benzoyl isocyanate the formation of adducts having the 1 : 2 composition is followed by the intramolecular substitution of the phosphorodithioate fragment under the influence of the siloxane or silazane groups. In the former case the cyclisation is accompanied by decarboxylation and leads to 6-oxo-2,4-diphenyl-1,3,5-oxadiazine (LXIV)—this is the main pathway. In the latter case the product is the benzoyl isocyanate dimer (LXV). The phosphorodithioate anion isomerises and is converted into the corresponding *S*-alkyl ester:[126]



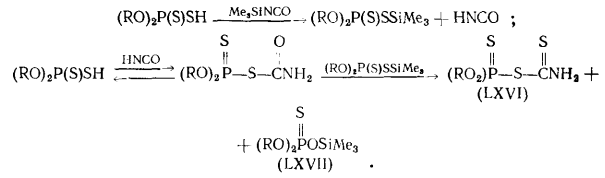
Cyclic silyl phosphorodithioates react with aryl and acyl isocyanates via the mechanism of the O,S-exchange process:[126]



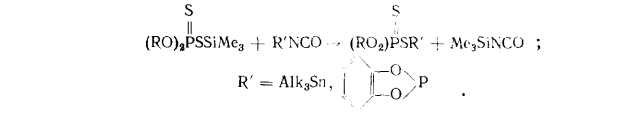
R = Ph, $Cl_3CC(O)$, PhC(O) .

Silyl phosphorodithioates do not add to isocyanatosilanes; apparently the steric and electronic influences of the trimethylsilyl group in the heterocumulene prevent the stabilisation of the adduct via the S → N migration of the thiophosphoryl group.

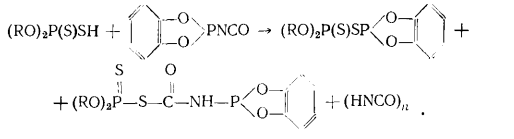
Phosphorodithioic acids readily rupture the Si–N bond in the trimethylsilyl isocyanate molecule and the subsequent reactions result in the formation of *S*-thiocarbamoyl phosphorodithioate (LXVI) and *O*-silyl phosphorothioate (LXVII):[127]



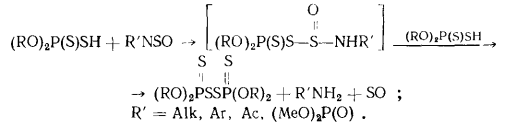
The interaction of silyl phosphorodithioates with other organoelemental isocyanates, namely isocyanatostannanes and phosphoroisocyanatidites, proceeds with cleavage of the element–nitrogen bond:[128]



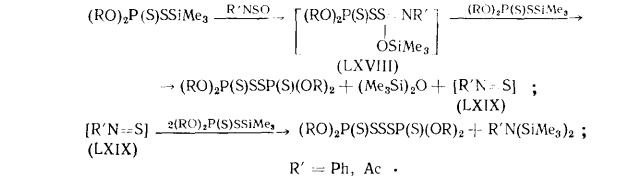
Both addition and substitution take place in the reactions of phosphorodithioic acids with *o*-phenylene phosphoroisocyanatidite:[128]



Significant differences in the chemical behaviour of silyl phosphorodithioates and phosphorodithioic acids have been observed also in their reactions with sulphinylamines. The reactions with phosphorodithioic acids result in the formation of bis(dialkylthiophosphoryl) disulphide, sulphur monoxide, and the corresponding amino-derivative:[129]



Silyl phosphorodithioates initially add to the S=O bond of the sulphinyl amine. The resulting intermediate (LXVIII) interacts with a second molecule of the phosphorodithioate to form bis(dialkylthiophosphoryl) disulphide, hexamethyldisiloxane, and an unstable intermediate (LXIX) having the thionitroso-structure, which reacts with two molecules of the silyl phosphorodithioate to form bis(thiophosphoryl) trisulphide and a disilylated amine:[130]

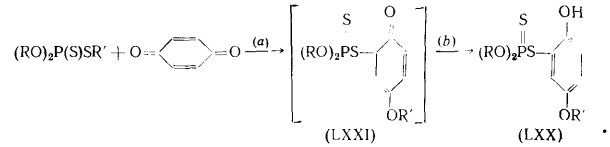


Thus the differences in the mode of reaction of silyl phosphorodithioates and phosphorodithioic acids with sulphinylamines are associated primarily with the different structures of the intermediates formed initially: phosphorodithioic acids form adducts involving the S=N bond, while silyl phosphorodithioates add to the S=O bond of the heterocumulene molecule.

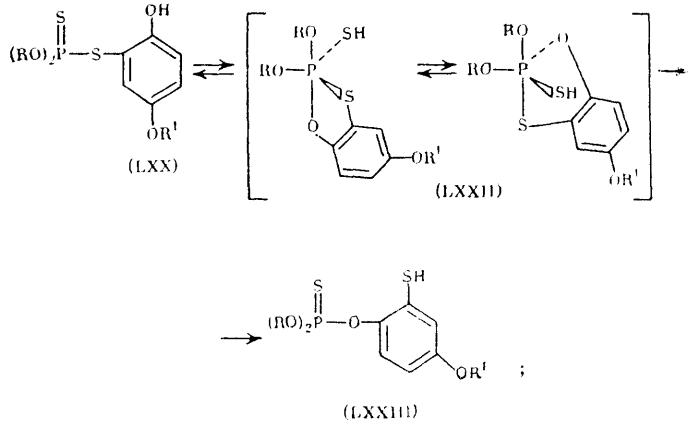
4. Reactions with *p*-Quinones

Like phosphorodithioic acids,[122] *S*-trimethylsilyl phosphorodithioates[131] are capable of adding readily to *p*-quinones, having a rigidly fixed *s*-transdisposition of the C=C and C=O bonds. The reactions with *p*-benzoquinone proceed vigorously in the absence of catalysts and are accompanied by the quantitative formation of *S*-aryl phosphorodithioates.

Kinetic study of these processes in various solvents using deuterated reactants showed[132] that both phosphorodithioic acids and their silyl esters initially react with *p*-benzoquinone to form 1,4-adducts (LXX). In non-polar weakly basic media the first stage of this reaction (*a*) determines the rate of the entire process ($k_H/k_D = 1$ for *p*-benzoquinone) and phosphorodithioic acids are therefore more reactive than silyl phosphorodithioates. With increase of the degree of nucleophilicity of the solvents, the proton transfer from the aromatic ring of the intermediate (LXXI) to the carbonyl group [stage (*b*); k_H/k_D is much greater than unity] becomes rate-limiting. The rates of reaction of phosphorodithioates (R′ = H or $SiMe_3$) are approximately the same under these conditions:



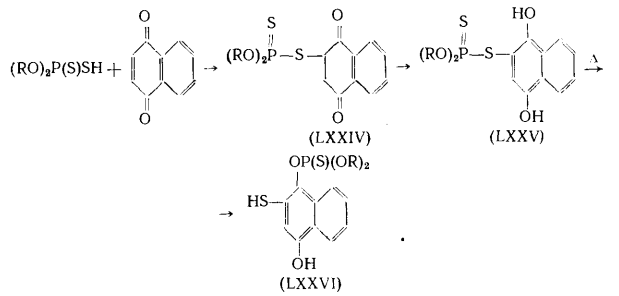
On vacuum distillation or heating, *S*-aryl phosphorodithioates (LXX) isomerise to the corresponding phosphoromonothioates.[131,132] The mechanism of their rearrangement includes the intermediate formation of mercaptophosphoranes (LXII):



R = H, Me_3Si.

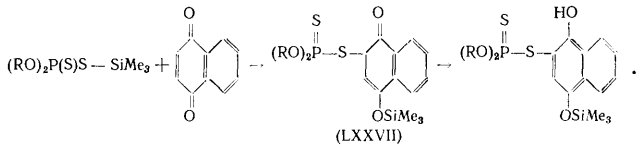
Kinetic study of the isomerisation,[132] occurring via a unimolecular mechanism, showed that the influence of the nature of the substituents at the phosphorus atom is determined by a set of electronic and steric factors and is described satisfactorily by the rules of the "hydroxyphosphorane concept".[133] The introduction of a phosphorus atom into the dioxaphospholan ring accelerates the isomerisation reaction so much that the phosphorodithioate adduct having the structure (LXX) cannot be isolated—the phosphoromonothioate (LXXIII) is formed immediately. This effect is associated with the low energy of the intermediate cyclic spiro-mercaptophosphoranes (LXXII) with R = $CH(CH_3)CH(CH_3)$. It is known[133–136] that spirocyclisation favours all prototropic processes involving the formation of hydroxyphosphoranes.

The interaction of phosphorodithioic acids and silyl phosphorodithioates with *p*-naphthoquinone proceeds via a mechanism formally analogous to that of the reaction with *p*-benzoquinone. However, detailed analysis of the changes in the infrared spectra of mixtures of solutions of *p*-naphthoquinone and a phosphorodithioic acid in CCl_4 as a function of time showed that the product of addition to the C=C bond of the quinone (LXXIV) is formed initially and is then gradually converted into the dithiophosphorylated dihydroxynaphthalene (LXXV).[137] Under severe conditions (100 °C), the phosphorodithioate isomerises to the phosphoromonothioate (LXXVI):[132]



(LXXIV) (LXXV) (LXXVI)

In the case of silyl phosphorodithioates the 1,4-adduct (LXXVII) is an intermediate, as in the reaction with *p*-benzoquinone:



(LXXVII)

Consequently the mechanism of the reactions of phosphorodithioic acids with *p*-quinones depends on the structure of the unsaturated reactant; silyl phosphorodithioates form initially 1,4-adducts in all cases.

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Summarising the discussion of the reactivity of organosilicon derivatives of phosphorus in addition reactions, one should note that the introduction of the trialkylsilyl group into the molecule of a phosphorus-containing system introduces significant, sometimes radical, changes into the character of Ad processes. The knowledge and purposeful employment of the specific features of the chemical behaviour of phosphorus–silicon reagents makes it possible to synthesise successfully new types of organoelemental compounds, which promotes the development and interpenetration of the chemistry of phosphorus and the chemistry of silicon.

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Ul'yanov-Lenin Kazan State University

Translated from *Uspekhi Khimii*, 53, 1709-1739 (1984) U.D.C. 542.91.632.936.2

The Synthesis of Mono- and Sesqui-terpene Insect Pheromones

A.M.Moiseenkov, K.V.Lebedeva, and B.A.Cheskis

The review presents a critical discussion of the available information on the syntheses of isoprenoid insect pheromones. Attention is concentrated on modern methods for the construction of molecules with a specified carbon skeleton. The efficiencies of the synthetic schemes are compared on the basis of the number of stages and the overall yields of the desired products. A systematic account of the data is given in terms of the types of pheromones.
The bibliography includes 179 references.

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I. INTRODUCTION

One of the most interesting and important fields in the modern science of life involves the study of insect pheromones. The term "pheromones" was proposed in 1959 [1] for chemical compounds "produced by living organisms, released into the environment, and inducing a specific response in individuals of the same biological species receiving them". Chemical signals ensuring intercommunications between insects may be individual compounds, but in most cases they are complex synergistic mixtures of substances whose biological activity can be reduced sharply following the removal of one of the components. The geometry and chirality of these components frequently exert a definite influence on the biological activity. The progress achieved recently in the determination of the absolute configurations of chiral pheromones has been possible by virtue of the employment of the most sophisticated methods of modern fine organic synthesis. Comparison of the spectroscopic characteristics and biological properties of the synthetic and natural specimens frequently permits a correct conclusion about the structure of the pheromone even in the presence of vanishingly small amounts of the latter.

Pheromones serve the most varied spheres in the vital activity of insects: sex and aggregation pheromones, fear pheromones, track pheromones, territorial markers, etc. are known. [2] The enormous interest by chemists and biologists in these copounds is associated not only and not so much with their purely scientific value as with the real possibility of their practical employment for the control of the size of the populations of harmful insects or as a method of fighting them by mass capture and, more rarely, by disorientation. At the present time there is a large number of reviews and monographs devoted to various questions concerning insect pheromones. [3-17] Correspondingly extensive factual data have accumulated on the syntheses of these compounds and are contained in a series of reviews, [13,18,19] which, being extremely extensive, nevertheless are not exhaustive, which has in turn led to the appearance of a series of small specialised reports on this topic. [20-23]

The present review is devoted to the synthesis of mono- and sesqui-terpene insect pheromones. Despite the fact that such data are partly contained in the communications noted above, there are no publications surveying the available information on this question. The present review contains data obtained mainly during the last ten years (up to July 1982 inclusive) and is concerned solely with regular and isomeric isoprenoid structures.

II. SEX AND AGGREGATION PHEROMONES

The sexual pheromones (SP) are produced by the insect in order to attract individuals of the opposite sex with the aim of subsequent coupling. Aggregation pheromones (AP) attract both sexes, which also as a rule precedes coupling. Since the purpose of the given group of substances is closely related to the propagation of the genus, they have in fact found extensive application in the protection of plants against insect pests and have therefore been studied at the present time on an extremely broad front.

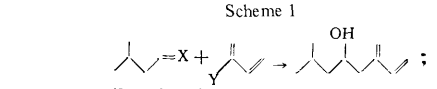
Among the isoprenoid SP, the main place is occupied perhaps by the monoterpenols found in certain insects of the family *Scolytidae*, which are dangerous forest pests.

1. Ipsenol

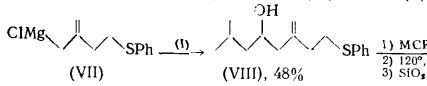
Ipsenol (VI) is a pheromone or a component of the pheromone mixture in many species of bark beetles of the genus *Ips* [24-29] and scolytid beetles of the genus *Pityokteines*. [30,31] In many instances only the *S*-(-)-enantiomer is biologically active. [28,31,32] Very many studies have been devoted to the synthesis of compound (VI). Here and henceforth we shall consider initially the preparation of the racemic product and then of the chiral derivative.

The majority of the methods of synthesis of compound (VI) are based on the construction of the whole C_{10} molecule from two C_5-synthones, one of which is isovaleraldehyde (I) or its dithioacetal (II) (Scheme 1).

Scheme 1



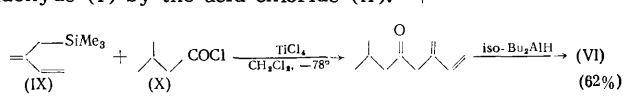
(I) X=O, (II) X = $S(CH_2)_2S$, (III) Y = H, (IV) Y = Br, (V) Y = $SnMe_3$;



Thus the deprotonation of the latter compound and subsequent alkylation with the bromide (IV) give rise to a product, which is converted into the required compound

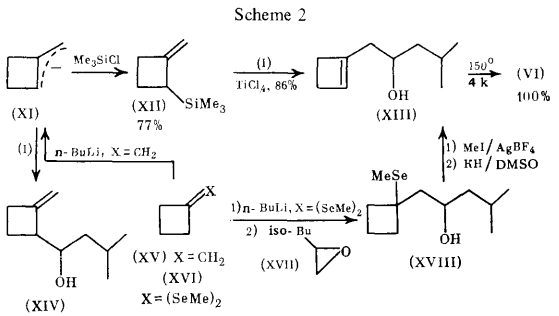
(VI) after the removal of the protecting dithio-group and hydride reduction.[24,33]

The bromide (IV) could not be converted into the magnesio- or lithio-derivative,[33] while the chloromagnesio-derivative (VII) could be very readily obtained from the corresponding chlorothioether, which made it possible to obtain the hydroxythioether (VIII), whose conversion with the aid of *m*-chloroperbenzoic acid (MCPBA) into the sulphoxide and the subsequent thermolysis of the latter yielded compound (VI) in an overall yield of 17%.[34] The single-stage synthesis of compound (VI), consisting in the Reformatskii condensation of compounds (I) and (IV) in the presence of zinc,[35] is extremely effective (yield 52%) and apparently the most appropriate method. The corresponding organozinc reagent could be conveniently generated *in situ* from tribromoisoprene.[36] The synthesis of compound (VI) with the aid of the ene reaction of compound (I) with isoprene (III), catalysed by Me_2AlCl, is also attractive by virtue of its simplicity and the ready availability of the starting materials.[37] However, the process is complicated by the concominant formation of the corresponding heterodiene condensation products. A single-stage synthesis of compound (VI) has also been achieved[38] using stannane (V). The use of the related silane (IX) gives an extremely low yield of compound (VI), but this limitation has been obviated by replacing the aldehyde (I) by the acid chloride (X).[39]†



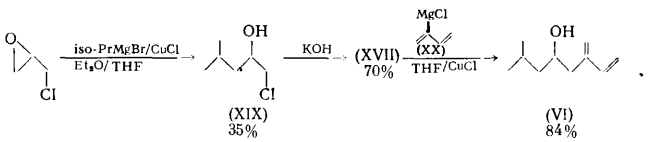
In one of the instances examined above, the 1,3-diene system is introduced into the molecules of compound (VI) in a "masked" form.[34] The same principle, but in a different version, underlies many syntheses of compounds (VI) based on cyclobutane derivatives (Scheme 2). Thus the ambident anion (XI), obtained by the deprotonation of methylenecyclobutane (XV), is converted in 80% yield into a mixture of the regioisomers (XIII) and (XIV) (~1:2) on treatment with the aldehyde (I); the thermolysis of cyclobutene (XIII) gives a quantitative yield of compound (VI):[40]

Scheme 2



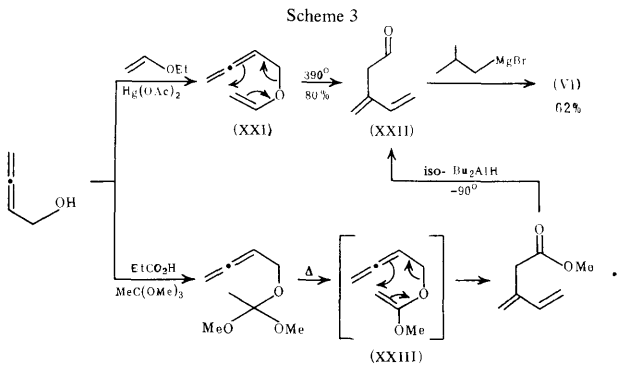
The isomer (XIV) remains a ballast compound under these conditions and its chromatographic separation is fairly difficult. A more effective procedure consists in the initial silylation of compound (XI) to give compound (XII), which subsequently reacts with compound (I) with total allyl rearrangement and gives rise to compound (XIII).[41] The third method of synthesis of this cyclobutene consists in the employment of the readily available *gem*-diselenide (XVI) as the C_4-synthone. Its metallation and treatment with the epoxide (XVII) (the C_6-synthone) lead to the hydroxyselenide (XVIII). The conversion of the latter into the dimethylselenonium derivative and its treatment with KH in dimethyl sulphoxide (DMSO) result in an exceptionally regiospecific formation of compound (XIII).[42] Overall, this method, being extremely laborious, is nevertheless characterised by a fairly high overall yield of compound (VI) (>50%).

The scheme involving the construction of the molecule of compound (VI) by coupling the epoxide (XVII) and buta-2-dienylmagnesium chloride (XX) as the C_6- and C_4-synthones respectively appears very simple and logical.[43] An extremely convenient method of synthesis of compound (XVII) proved to be the condensation of epichlorohydrin with isopropylmagnesium bromide in the presence of one equivalent of CuCl via the stage involving the formation of the intermediate chlorohydrin (XIX); the use of CuCl also makes it possible to increase significantly the yield of compound (VI) in the next stage:[44]



The same principle of the two-synthone approach is illustrated by Scheme 3. Here the key operation is the formation of the dienal (XXII) by the Claisen rearrangement of the vinylallenic ethers (XXI)[45] or (XXIII).[46] In both cases the overall yield of compound (VI) reaches 35%.

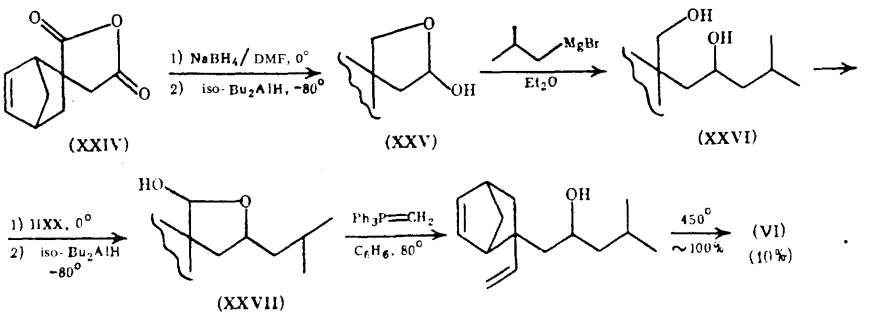
Scheme 3



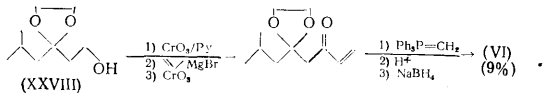
The synthesis of compound (VI) from itaconic anhydride in the form of its adduct (XXIV) with cyclopentadiene (Scheme 4) is somewhat less effective.[47] The main strategy reduces in this instance to the selective transformation of compound (XXIV) into the hemiacetal (XXV) and subsequently to the just as selective oxidation of the 1,4-glycol (XXVI) with the aid of pyridinium chlorochromate (PCC) to the lactol (XXVII). The methylenation of the latter and the retrodiene removal of the protection of the initial *exo*-methylene bond lead ultimately to compound (VI) in a very moderate yield:

†Here and henceforth the overall yields are indicated in brackets.

Scheme 4

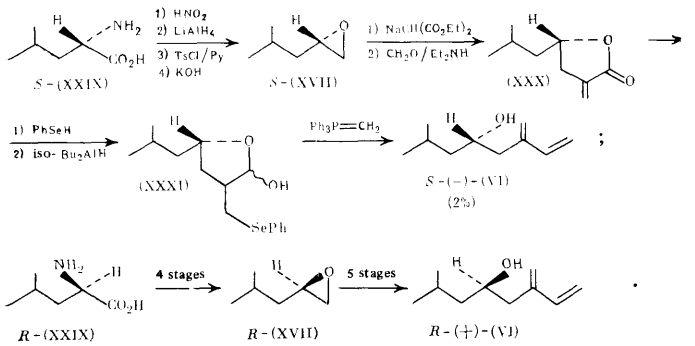


The overall yield in the six-stage synthesis of compound (VI) from the hydroxyacetal (XXVIII) with the aid of traditional methods for the increase in the length of the isoprenoid chain proved to be just as low: [48]



The synthesis of optically active compound (VI), which has been achieved in a low yield but which has made it possible to establish the absolute configuration of the pheromone, was undertaken from *S*-(+)-leucine (XXIX) (Scheme 5). Here the key product was the chiral epoxide *S*-(XVII) obtained in four stages. Its condensation with diethyl malonate and subsequent methylenation give rise to the lactone (XXX), which is transformed into the lactol (XXXI) after the protection of the *exo*-methylene double bond. Its Wittig methylenation, which takes place with the simultaneous removal of the phenyl selenide protecting group, leads to the natural product *S*-(-)-(VI). [49,50] The enantiomer *R*-(+)-(VI) has been obtained analogously from *R*-leucine (XXIX) via *R*-(XVII). [50]

Scheme 5



Subsequently both enantiomers (VI) were synthesised via a shorter pathway, using the method described above, [43] from the same chiral epoxides (XVII) and butadienylmagnesium chloride (XX) in an overall yield of ~50%. [51]

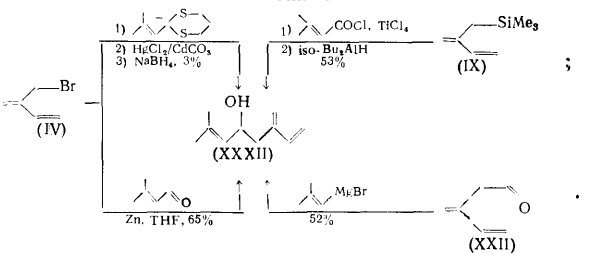
It is of interest to note that the biological action of the natural product *S*-(-)-(VI) is not inhibited by the presence of its optical isomer *R*-(+)-(VI), [28,31] at least for the bark beetle *Ips grandicollis* and the scolytid beetle *Pityokteines curvidens*. This fact permits one to hope for a possible practical application of compound (±)-(VI), which will thus remove the necessity for its enantioselective synthesis.

2. Ipsdienol

Like its dihydro-derivative (VI), ipsdienol (XXXII) is an aggregation-sex pheromone in many *Ips* [24-27,29,52-57] and *Pityokteines* [30,31] species and, in contrast to compound (VI), these functions can be fulfilled by both enantiomers of compound (XXXII) (see, for example, Vité et al. [32]).

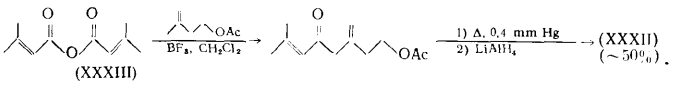
In conformity with the evident structural characteristics of this compound, the strategy used in many of its total syntheses proved to be analogous to that already considered for ipsenol (VI). Thus the two-synthone approaches ($C_5 + C_5$ or $C_4 + C_6$), represented in Scheme 6, are widely used:

Scheme 6



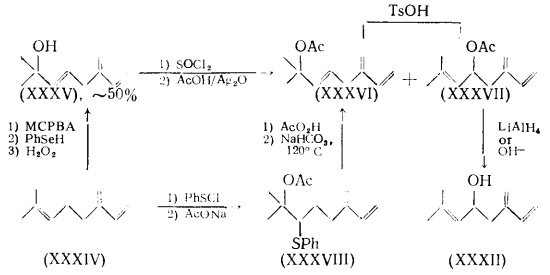
The extremely low overall yield of compound (XXXIII), initially obtained in three stages from the bromo-derivative (IV), can apparently be accounted for by the authors' [24,33] endeavour to confirm in the first place the structure of this pheromone. On the other hand, the simplicity and effectiveness of the synthesis of compound (XXXII) by the Reformatskii method [36,58] as well as the syntheses from the silane (IX) [39] and the aldehyde (XXII) [45,46] are evident.

The method based on the condensation of the anhydride (XXXIII) with isopentenyl acetate [59] proved to be fairly apt, despite the formation of up to 30% of regio-isomers as side products in the first stage:



A fundamentally different approach, directed in essence to the selective hydroxylation of myrcene (XXXIV), which possesses the fundamental structural features of the molecule of compound (XXXII), is illustrated in Scheme 7:

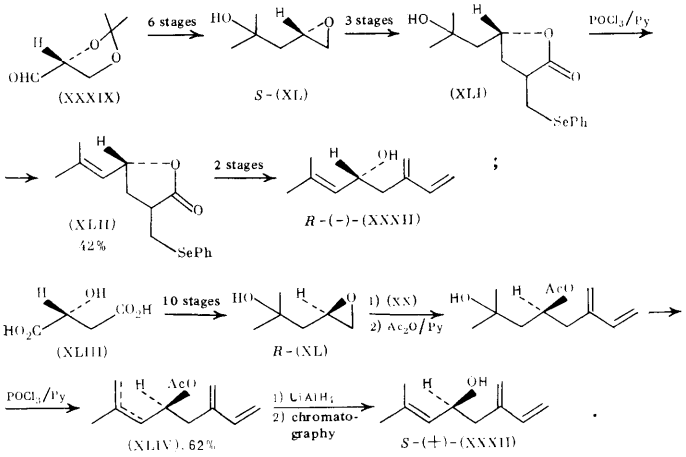
Scheme 7



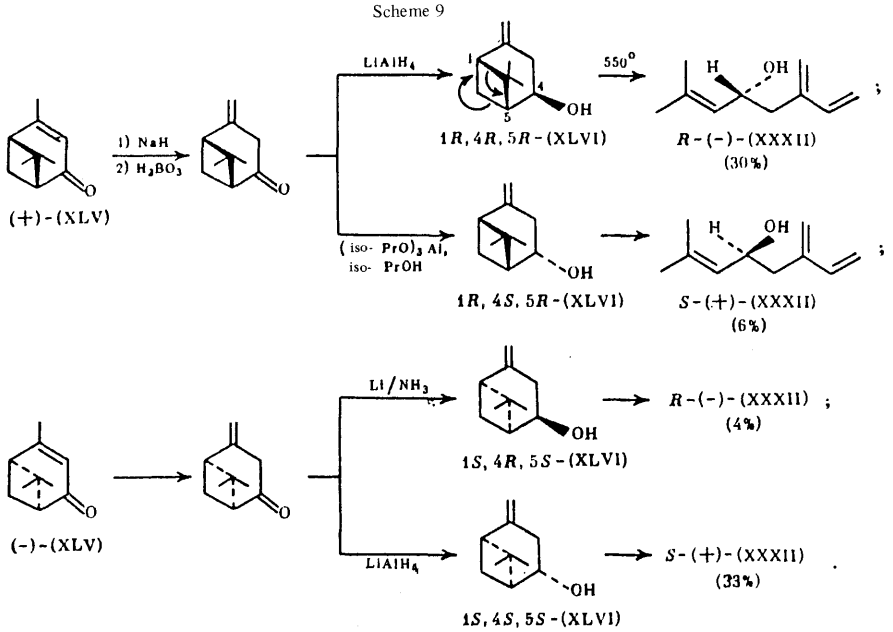
Thus the selective epoxidation of compound (XXXIV) with subsequent opening of the epoxide ring with the aid of PheH and treatment of the intermediate hydroxyselenide with H_2O_2 gives rise ultimately to amitinol (XXXV), which has proved to be the component of the aggregation pheromones (AP) of the bark beetles (see below). In view of its lack of resistance to the action of acids, the direct rearrangement of the tertiary alcohol (XXXV) proved difficult. An indirect procedure was therefore undertaken: the tertiary alcohol (XXXV) was converted into a mixture of the acetates (XXXVI) and (XXXVII); the latter was isolated from the mixture by the reductive cleavage with lithium tetrahydroaluminate to give the alcohols (XXXV) and (XXXII); and by the selective acetylation of the secondary alcohol (XXXII) with acetic anhydrides and the subsequent chromatography of the mixture of compounds (XXXV) and (XXXVII); the racemic secondary alcohol (XXXII) was obtained from the acetate (XXXVII) in an overall yield of ~10%. [60] A related approach consists in the selective conversion of compound (XXXIV) into the acetoxysulphide (XXXVIII) and the conversion of the latter into the acetate (XXXVII) via the sulphoxide and the tertiary acetate (XXXVI), which smoothly rearranges to compound (XXXVII). [The use of the rearrangement (XXXVI) → (XXXVII) would have probably halved the number of stages in the preceding synthesis.] The hydrolysis of compound (XXXVII) affords the required compound (XXXII) in an overall yield of ~25%. [61]

By analogy with the syntheses of the enantiomeric compounds (VI), the optically active isomers of compound (XXXII) have been obtained via the chiral hydroxyepoxides (XL) (Scheme 8). [51,62] Here compound *S*-(XL) was synthesised from a derivative of *R*-glyceraldehyde (XXXIX), which can be obtained in its turn from D-mannitol. The enantiomer *R*-(XL) was prepared from *R*-malic acid (XLIII). The conversion of the epoxide *S*-(XL) into the alcohol *R*-(XXXII) involves the formation of the selenide (XLI) at an intermediate stage (see Scheme 5). Its dehydration leads to the olefin (XLII), whose further transformation into the required compound *R*-(XXXII) was achieved analogously to the synthesis of compound (VI) via Scheme 5 in an overall yield of 0.2% with respect to compound (IX). The enantiomer *S*-(XXXII) was synthesised from the epoxide *R*-(XL), which was condensed by the method described above [43] with butadienylmagnesium chloride (XX). Successive acetylation of the secondary hydroxyl and dehydration lead to a ~1 : 1 mixture of the allyl isomers (XLIV). The absence of regioselectivity at the given stage is undoubtedly a significant disadvantage of the approach considered, because it requires the chromatographic isolation of compound *S*-(XXXII), formed after the reduction of the acetate in an overall yield of 0.03%.

Scheme 8



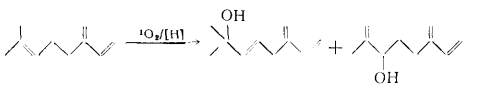
Scheme 9



An elegant method of synthesis of both enantiomers of compound (XXXII) is based on the four-stage transformation of the optically active verbenones (XLV) (Scheme 9). The β-verbenols (XLVI), obtained by the reduction of the corresponding non-conjugated ketones, were subjected to flash pyrolysis. As a result of the opening of the four-membered ring, the 1,5-diastereoisomers are then converted in pairs into the required compound (XXXII) in approximately identical yields, retaining the absolute configuration of the chiral centre C(4) in the molecule of compound (XLVI).[63] A disadvantage of this scheme is the comparative difficulty of obtaining the optically active verbenones (XLV).

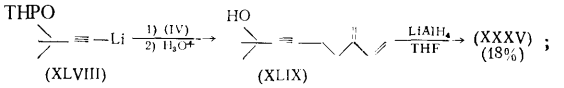
3. Amitinol

Yet another representative of the linear monoterpenols entering into the composition of the AP of the bark beetle of the genus *Ips* is amitinol (XXXV).[29,64] Apart from the synthesis described above (Scheme 7),[60,61,65] there exists yet another method of obtaining compound (XXXV) from myrcene, which consists in its reductive photochemical oxidation in the presence of $(H_2N)_2CS$ [66] or $n\text{-}Bu_4NBH_4$.[67] The regioisomer (XLVII) formed simultaneously can be separated chromatographically with comparative ease. The preparatively more convenient method employing $n\text{-}Bu_4NBH_4$ [67] is characterised by a somewhat lower yield of compound (XXXV):



(XXXIV) (XXXV) (XLVII)
40—50% 30—40%

A two-synthone ($C_5 + C_5$) scheme has also been described for the construction of amitinol from the bromo-derivative (IV) and the acetylide (XLVIII) with subsequent hydride reduction of the intermediate carbinol (XLIX).[45] However, one should note the moderate overall yield of compound (XXXV) in this instance:



(XLVIII) (XLIX)

THP = tetrahydropyranyl.

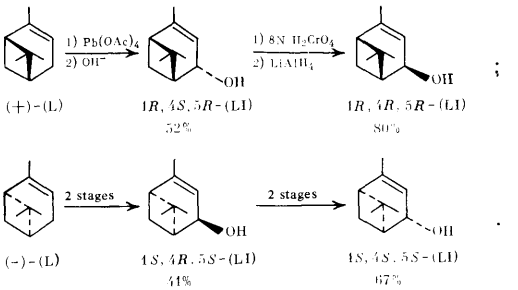
Finally, the pheromone (XXXV) has been recently identified[29] in one of the bark beetle species and has been obtained by the allyl isomerisation of ipsdienol on treatment with 3% HBF_4; the authors unjustifiably assumed that compound (XXXV) had not been synthesised previously.

4. Verbenols

The *cis*- and *trans*-verbenols (LI) have been found in the AP of many species of the *Ips* bark beetle and the timber beetles *Dendroctonus* [24—26,56,68—70] and in many instances the biological action of compounds (LI) can depend significantly on their enantiomeric purity;[26,32,71—73] mainly the 4*S*-(-)-*cis*- and 4*R*-(+)-*trans*-verbenols are active.

The syntheses of the racemic and chiral compounds (LI) are fairly isotypical and are based on standard and thoroughly investigated transformations of the α- and β-pinene derivatives.[24,33,63,74,75] In particular, the chiral compounds *trans*-(LI) have been obtained by the allyl oxidation of the corresponding α-pinene (L) enantiomers and *cis*-(LI) have been synthesised by the Jones oxidation of *trans*-(LI) to the verbenols (XLV) with a subsequent hydride reduction[74,75] (Scheme 10).

Scheme 10



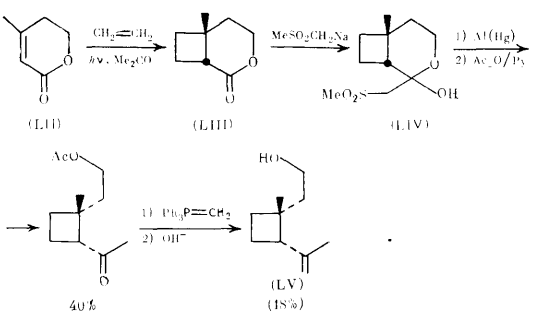
The partial racemisation occurring during the synthesis of the verbenols can be compensated by their conversion into the D-3β-acetoxyetienic esters and by the improvement of the optical purity of the latter as a result of crystallisation and the regeneration of the required alcohols with the aid of hydride reduction.[74,75]

5. Grandisol

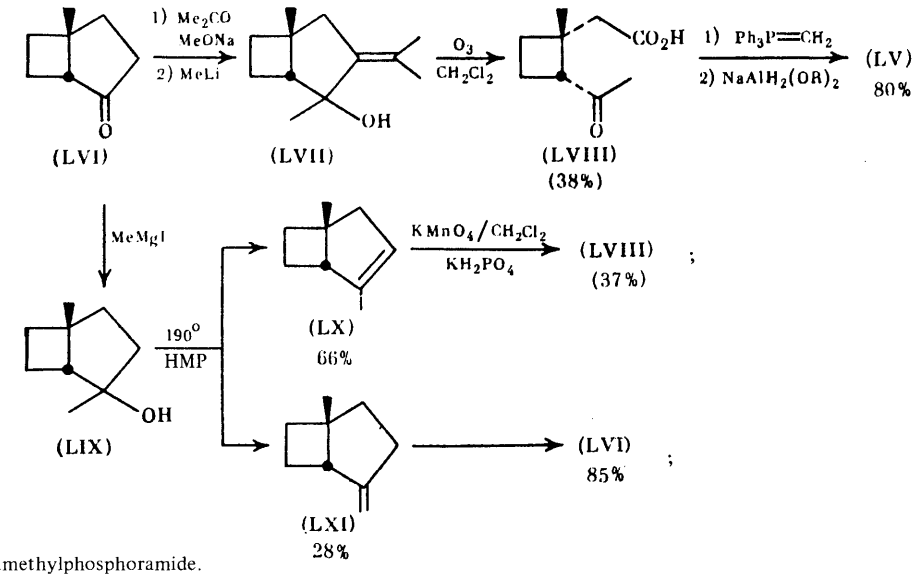
The snout beetle *Anthonomus grandis* is one of the most dangerous pests on the cotton plant, "eating up", for example, 300 million dollars annually on American farms.[76] The aggregation-sexual pheromone "grandlure", produced by the males of this insect, consists of four components, the principal component being (+)-grandisol (LV).[77] Its enantiomer also exhibits a high biological activity,[78] which apparently eliminates the necessity for the chiral synthesis of compound (LV) for practical purposes.

Numerous studies have been devoted to the synthesis of the racemate of compound (LV), evidently owing to the unusual nature of its cyclobutane structure and the growing need for this pheromone. Many methods for the construction of the molecule of compound (LV), developed prior to 1975, have been described in a review,[20] which effectively illustrates the evolution of the overall strategy in the synthesis of substances of this type. We shall therefore consider below only recently published and the most promising of the proposed schemes.

The key stage in the majority of the methods is the formation of the cyclobutane fragment of the molecule of compound (LV) and this is usually achieved by the photochemical [2 + 2]-cycloaddition. Thus the photoadduct (LIII) has been obtained from the lactone (LII) and ethylene; its treatment with the sodium derivative of dimethyl sulphone gives rise to the sulphone (LIV), which has been converted into grandisol by means of four simple operations:[79]



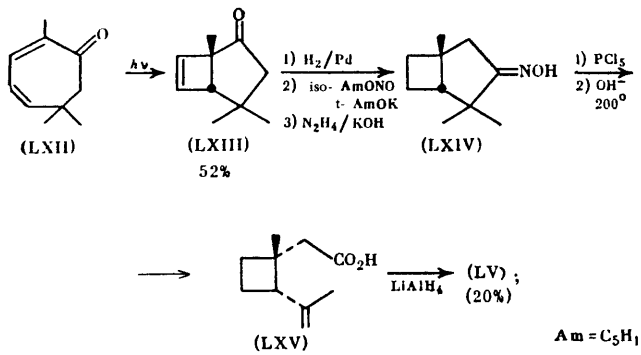
Scheme 11



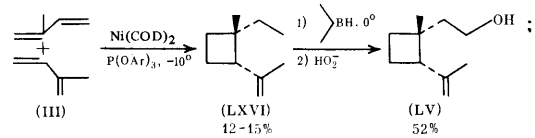
HMP = hexamethylphosphoramide.

The syntheses of compound (LV) based on the use of 3-methylcyclopentenone instead of the lactone (LII) (Scheme 11) can be regarded as just as successful. Here the main task is the specific transformation of the cyclopentane fragment of the photoadduct (LVI). In one instance this has been achieved by its conversion into the isopropylidene-carbinol (LVII) and subsequent ozonolysis to the ketoacid (LVIII) [80] and in another instance by the dehydration of the alcohol (LIX) to the olefins (LX) and (LXI). The oxidative cleavage of the first of these leads to the same ketoacid (LVIII) as above, while the cleavage of the second results in the formation of the initial ketone (LVI). [81]

A novel and extremely effective synthesis of compound (LV) is based on the intramolecular photocyclisation of the readily available eucarvone (LXII). The main difficulty in this approach consists in the shift of the carbonyl functional group in the intermediate (LXIII) to the neighbouring secondary carbon atom, which is achieved by hydrogenation and nitrosation. The subsequent reduction leads to the saturated oxime (LXIV). The Beckmann rearrangement of this kind and hydrolysis of the intermediate nitrile afford the acid (LXV), which is reduced to (±)-grandisol: [82]

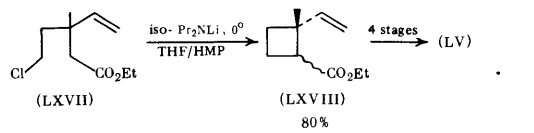


Apart from the photochemical methods, a whole series of fundamentally new approaches to the synthesis of compound (LV) have been described. The zerovalent nickel-catalysed cyclodimerisation of isoprene to the diene (LXVI) with subsequent selective "anti-Markovnikov" hydration of one of the C=C bonds must be regarded as the shortest of these, although its effectiveness is comparatively low: [83]



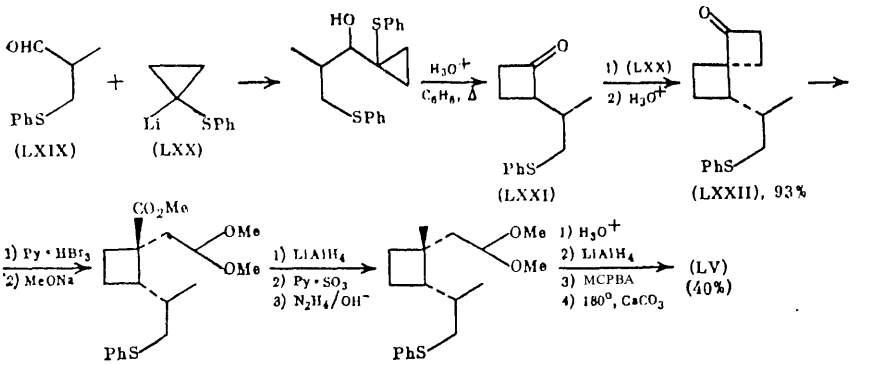
COD = cyclo-octadiene.

The construction of the cyclobutane skeleton of compound (LV) by the intramolecular cyclisation of suitable precursors with functional groups is usually associated with a low stereoselectivity of this key stage. Thus the smooth cyclisation of the δ-chloroether (LXVII) gives rise to a mixture of stereoisomers of compound (LXVIII) (*Z*/*E* ≅ 2:1); the subsequent conversion into compound (LV) entails a laborious operation involving their chromatographic separation. [84] The overall yield of compound (LV) was not indicated in the above study:

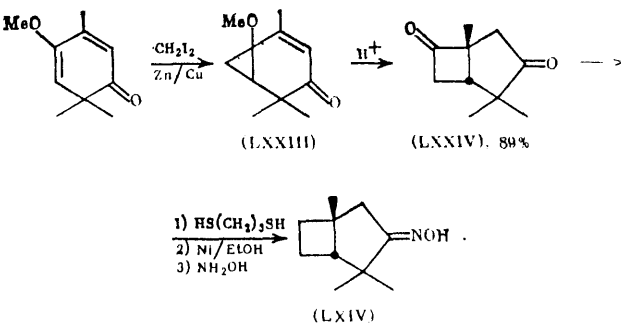


The cyclopropylcarbinyl rearrangement (CPCR) has served as an extremely effective procedure for the formation of the four-membered ring in the molecule of grandisol. The latter has been obtained (Scheme 12) in a very high yield and with a small admixture of the *E*-isomer (20%) from the thioaldehyde (LXIX) and the lithio-derivative (LXX) by the double application of the CPCR, which leads to the cyclobutanones (LXXI) and (LXXII). The required carbon skeleton was then obtained by the haloform cleavage of the spiro-heptanone (LXXII). The required product (LV) is then obtained by the reduction of the ester group to the methyl group and of the acetal group to the alcohol group, followed by the elimination of the elements of PhSH: [85,86]

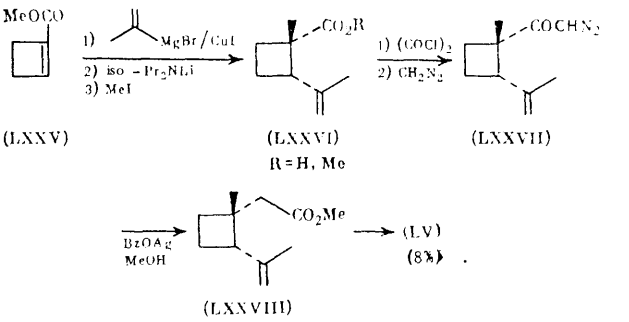
Scheme 12



An analogous principle underlies another approach leading to the geometrically pure compound (LV) in an overall yield of ~7%.[87] In this case the methoxybicycloketone (LXXIII) is subjected to the CPCR rearrangement and is transformed into the dione (LXXIV), which is then converted into the oxime (LXIV). The formation of compound (IV) from the oxime[82] was examined above:

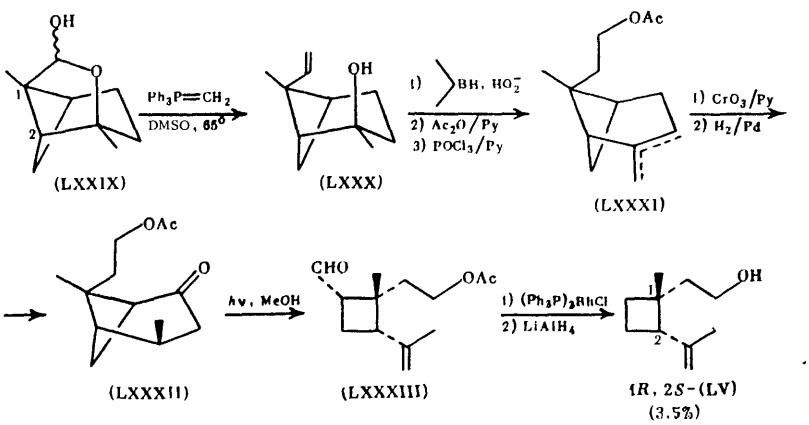


Among the syntheses of compound (LV) based on the use of cyclobutane precursors, mention should be made of the three-stage stereoselective transformation of the conjugated olefin (LXXV) into the ester (LXXVI). Its conversion into the diazoketone (LXXVII) and further into the ester (LXXVIII) makes it possible to obtain compound (LV) smoothly albeit in a low overall yield:[88]



The synthesis of (+)-grandisol (LV) is represented in Scheme 13. Its absolute 1*R*, 2*S*-configuration follows from the known configuration of the remote precursor (LXXIX), in the course of the transformation of which into the required compound the centres indicated are not involved.[89] The lactol (LXXIX), obtained in four stages from (-)-β-pinene, was converted by the Wittig reaction into the olefin (LXXX) and then by three simple operations into a mixture of the olefins (LXXXI). The allyl oxidation of this mixture with subsequent hydrogenation led to a satisfactory yield of the ketone (LXXXII). The Norrish photochemical cleavage of the latter, the deformylation of the aldehyde (LXXXIII) by means of Wilkinson's complex, and the removal of the acetate protecting group yield ultimately the optically pure 1*R*, 2*S*-(+)-grandisol, the biological and physicochemical properties of which correspond to those of the natural product.

Scheme 13



In another procedure (Scheme 14) both optical isomers of compound (LV) have been obtained from the racemic acid (LXXXIV), which can be readily synthesised from the cyclic photoadduct of ethylene with 3-ethoxycarbonylcyclopent-2-enone.[90] Quinine, cinchonine, or brucine salts of this acid have been separated and then converted in pairs into the isopropylidene derivatives (LVII) via stages involving the esters (LXXXV) and ketones (LVI). The conversion of compound (LVII) into the enantiomers of compound (LV) does not differ fundamentally from that considered in Scheme 11.

Naturally, neither of the enantioselective syntheses of compound (LV) is suitable for preparative purposes because of the large number of stages and the low overall yield, but the absolute configuration of this pheromone has been established with their aid.

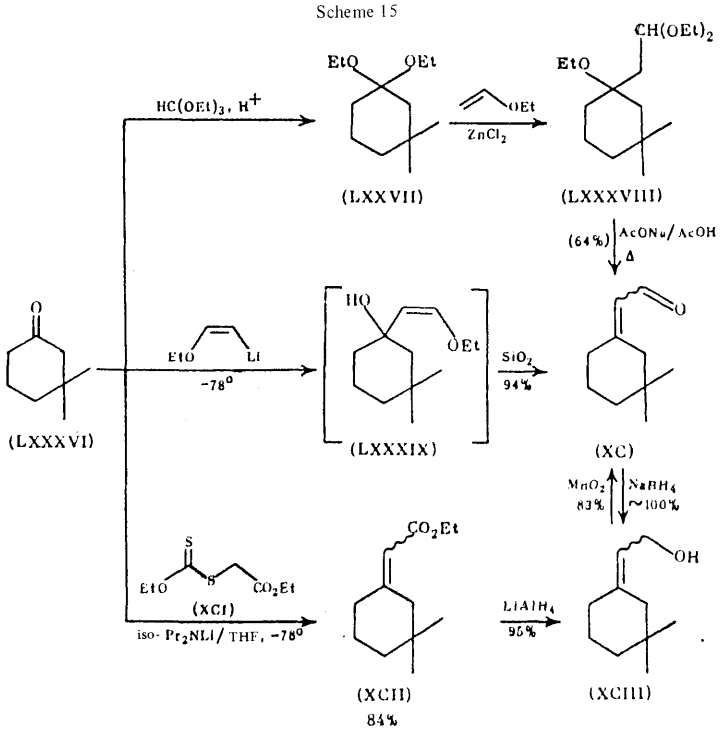
In conclusion one should mention the synthesis of 1*S*, 2*R*-(-)-(LV), carried out in order to investigate the biological properties of this enantiomer; this synthesis involves the separation of the quinine salts of the enantiomeric acids (LXV) obtained by the oxidation of compound (±)-(LV).[78]

From the wide variety of syntheses of compound (LV), one can apparently isolate the most promising syntheses based on the cyclodimerisation of isoprene[83] and the intramolecular photocyclisation of eucarvone.[82]

6. Cyclohexane Components of "Grandlure"

Apart from compound (LV), the cyclohexane monoterpenes *Z*,*E*-(XC) and *Z*-(XCIII) also enter into the composition of the AP of the cotton snout beetle. The methods of synthesis of these components of "grandlure" are fairly simple and have been largely considered in another review.[13] The majority of the procedures, including those published recently[91-93] (Scheme 15), are based on the employment of the readily available dimethylcyclohexanone (LXXXVI). The condensation of the acetal (LXXXVII) with ethyl vinyl ether gives a quantitative yield of the ethoxyacetal (LXXXVIII), which is subsequently converted into a mixture of the aldehydes (XC). The latter can be separated chromatographically and reduced to the corresponding isomers of the alcohols (XCIII).[91] The synthesis based on the condensation of the ketone (LXXXVI) with ethoxyvinyllithium must be included among the most effective methods. The resulting intermediate (LXXXIX) is smoothly converted into a 1:1 mixture of the isomers of compound (XC) in the course of chromatography of SiO_2.[92] A novel method of synthesis of αβ-unsaturated esters is characterised by high yields; the interaction of the carbanion derived from the dithiocarbonate (XCI) with the ketone (LXXXVI) leads to a ~1:1 mixture of the isomeric esters (XCII).[93] The latter can be reduced to the alcohols (XCIII), whose oxidation gives rise to the aldehydes (XC).[91]

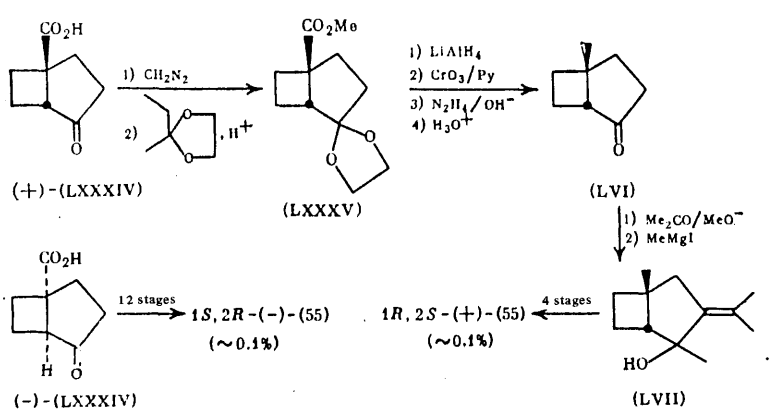
Scheme 15



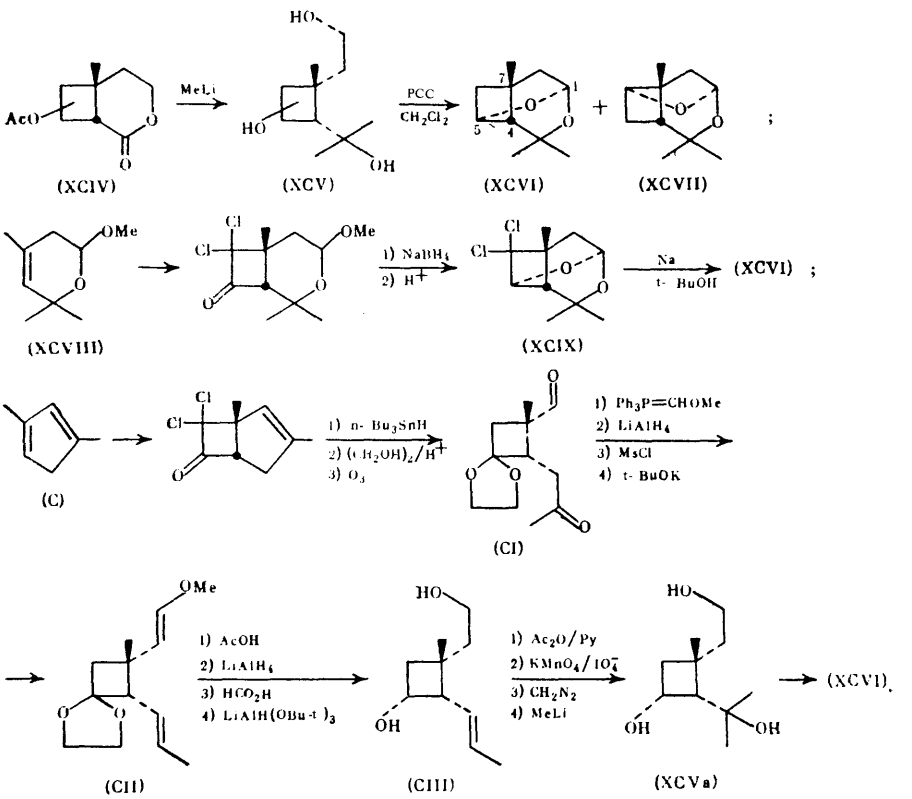
7. Lineatin

In contrast to the bark beetles of the genus *Ips*, in other representatives of this family (*Scolytidae*), namely the beetles *Trypodendron lineatum*, the AP, called lineatin, is produced by the females. It has been shown recently that the AP has the unusual dioxatricyclononane structure (XCVI).[94,95] It has also been established that the biological action of the natural (+)-isomer is not inhibited by its inactive optical isomer (-)-(XCVI).[96]

Scheme 14



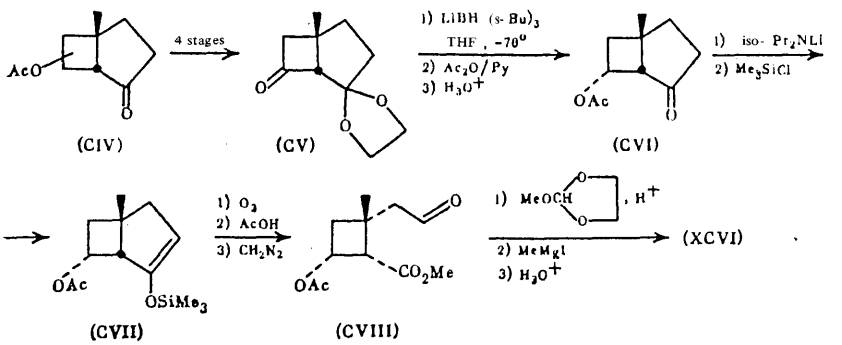
Scheme 16



In the first brief publication on the synthesis of compound (+)-(XCVI) three approaches, which must be regarded as extremely ineffective, are discussed at once. Nevertheless, they make it possible to establish unambiguously the structure of this pheromone[95] (Scheme 16). The cyclobutane fragment of the molecule of compound (XCVI) is then formed, as for compound (LV), by photocycloaddition. In one of the variants of the synthesis, when a mixture of the photoadducts (XCIV) of vinyl acetate and the lactone (LII) was employed, a mixture of the required compound (XCVI) and its regioisomer (XCVII), which can be separated chromatographically, was obtained via a stage involving the triols (XCV). In two other variants the transformation of the photoadducts of dichloroketen and the olefin (XCVIII) or the diene (C) led respectively to the acetals (XCIX) and (CI). The former was subsequently converted into compound (XCVI) by the reductive cleavage of the C–Cl bond, while the latter was converted by a multistage procedure, including the conversion into the vinyl ether (CII) and then into the diol (CIII). The latter was transformed in four stages into the required regioisomer of the triol (XCVa), whose oxidative cyclisation yielded the required compound (XCVI).

The approach involving the transformation of a 7:2 mixture of the photoadducts (CIV) of vinyl acetate and 3-methylcyclopent-2-enone [97] (Scheme 17) proved just as ineffective. Since it was found that the dominant regioisomer behaves as a ballast compound, the first four stages, including the chromatographic stage, reduced to the isolation of the required regioisomer in the form of the ketoacetal (CV). The latter is converted with the aid of a bulky reductant initially into the alcohol with the required *endo*-configuration and then into the ketoacetate (CVI) and the silyl ether (CVII). Its ozonolysis and treatment with acetic acid and then with diazomethane lead to the aldehyde (CVIII), which is transformed by three simple operations into the required compound (+)-(XCVI) in an overall yield of ~0.15%.

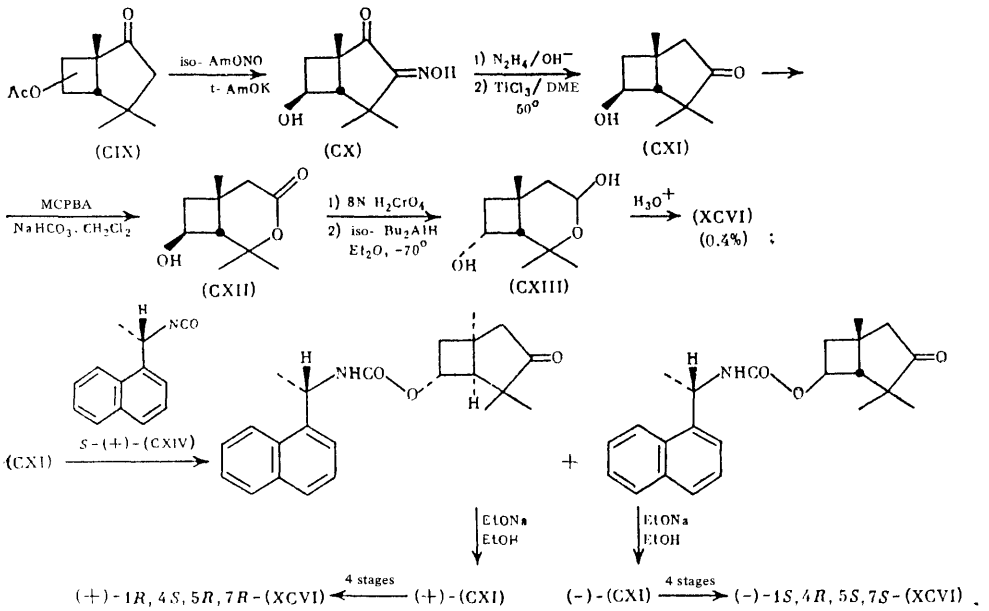
Scheme 17



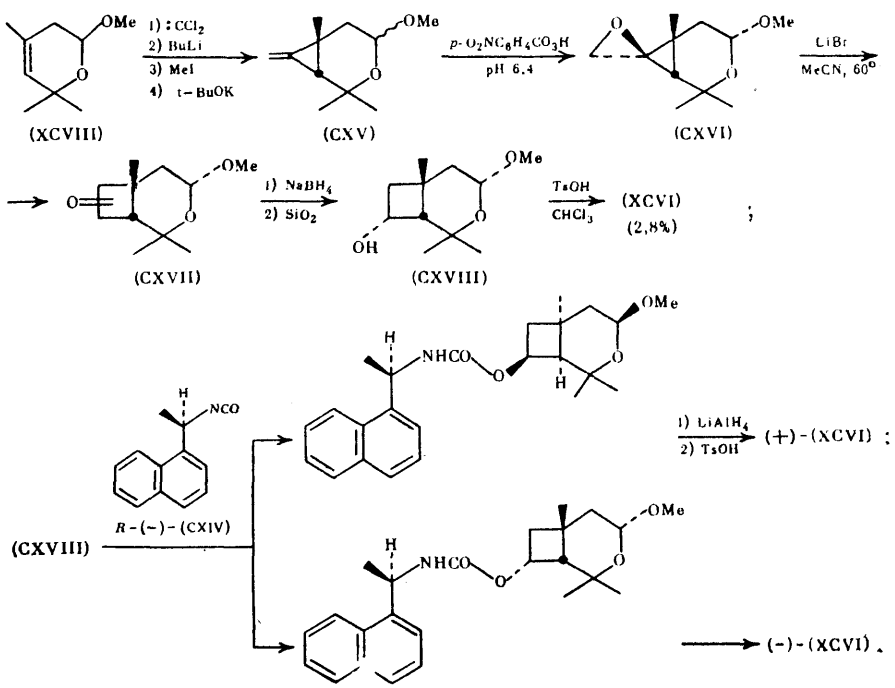
The synthesis of compound (±)-(XCVI) from the photoadducts of vinyl acetate and 2,4,4-trimethylcyclopent-2-enone, which is a mixture of the ketoacetates (CIX) in proportions of 3:2 with the required regioisomer predominating (Scheme 18), is significantly more successful. [98] In the first stage involving the "displacement" of the C=O group, the ballast isomer (CIX) is eliminated as a result of the retroaldol cleavage of the intermediate β-ketol and the oxime (CX) is converted in two stages into the ketoalcohol (CXI). The latter is transformed by the Baeyer–Villiger reaction into the lactone (CXII), whose conversion into the individual *endo*-isomer of the hydroxylactol (CXIII) is achieved by oxidation with subsequent reduction of the intermediate ketolactone with a bulky reagent. The acid-catalysed cyclisation of compound (CXIII) completes the sequence of reactions.

The synthesis of compound (±)-(XCVI) presented in Scheme 19 is even more effective. [99] The starting compound is the olefin (CXV), obtained in four stages from the dihydropyran (XCVIII). The conversion of this olefin into the epoxide (CXVI) and its subsequent rearrangement lead stereospecifically to the *endo*-isomers of the ketones (CXVII), the ratio amounting to 4:1 with the required isomer predominating. The latter is isolated chromatographically in the form of the alcohol (CXVIII) after the reduction of the mixture and is then cyclised to the required compound (XCVI).

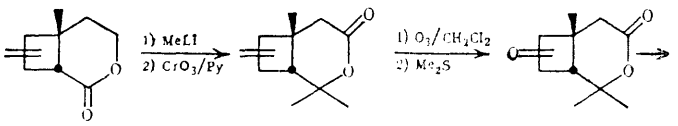
Scheme 18



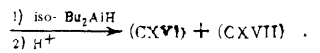
Scheme 19



The synthesis of the racemic compound (XCVI), based on the five-stage transformation of the photoadducts (CXIX) of an allene and the lactone (LII) (the mixture composition is 3:2 with the required isomer predominating) must be regarded as the most effective and shortest of the existing syntheses.[100] The conversion of the mixture of compounds (CXIX) into the olefins (CXX) and their subsequent ozonolysis afford the ketones (CXXI), which are converted, after reduction and cyclisation, into a ~2:1 mixture of the regioisomers (XCVI) and (XCVII). The required isomer (XCVI) is then isolated chromatographically in an overall yield of ~9%:



(CXIX) (CXX) 70% (CXXI) 69%



The method of synthesis of compounds (+)-(XCVI) via Scheme 20 [101] from the cyclic adducts of dichloroketen and isoprene, which are readily converted into the cyclobutanone (CXXII) in an overall yield of 39%, can also serve as a fairly effective preparative procedure. Condensation with acetone leads to the ketols (CXXIII), which are subjected to hydroboration, after reduction by a bulky reagent and protection of the secondary hydroxyl, with subsequent oxidation to the diols (CXXIV). The latter are transformed in two stages into the hydroxylactone (CXIIa), whose conversion into the required compound (XCVI) is analogous to that examined in Scheme 18.

The enantiomers of compound (XCVI) have been obtained by means of the chromatographic separation of the diastereoisomeric derivatives synthesised from the alcohol (CXI) and the *S*-(+)-isocyanate (CXIV) [98] (Scheme 18), from the alcohol (CXVIII) and compound *R*-(-)-(CXIV) [99] (Scheme 19), or from the alcohol (CXIIa) and the chiral hydroxylactone (CXXV), which can be obtained from *cis*-chrysanthemic acid[101] (Scheme 20). The subsequent regeneration of the optically active compounds (CXI), (CXVIII), or (CXIIa) and their transformation in the way described above lead to the enantiomers of compound (XCVI), among which the dextrorotary compound proved to be the natural product. X-Ray diffraction analysis of the diastereoisomers (CXXVI) made it possible to establish finally the absolute configurations of the pheromone and its optical isomer as 1*R*, 4*S*, 5*R*, 7*R* for (+)-(XCVI) and 1*S*, 4*R*, 5*S*, 7*S* for (-)-(XCVI).[101]

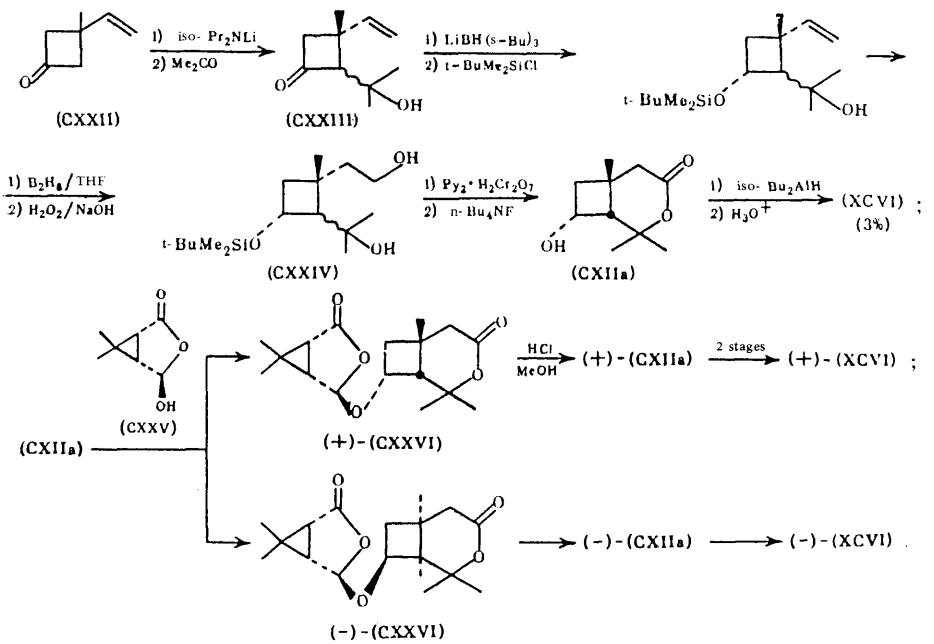
8. Periplanone B

The identification of the SP of the female of the American cockroach *Periplaneta americana* is an extremely complex chemical problem which has been recently solved successfully. As early as 1963, a structure was proposed for this pheromone[102] but it was subsequently disproved[103] and it was not until 13 years later that the structure of periplanone B (CXXX), one of the two main components of the pheromone mixture, was finally elucidated. It is a sesquiterpenoid of the germacrane series.[104-106]

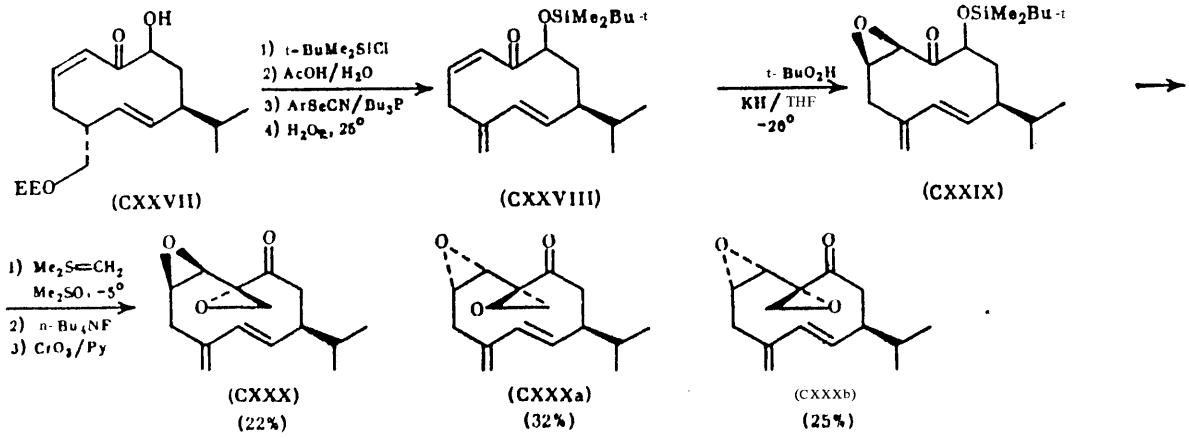
A very elegant, effective, and hitherto unique synthesis of this pheromone led to three of its four possible isomers and in addition made it possible to establish the relative configuration of periplanone B [107] (Scheme 21).

The norgermacrane ketodiol (CXXVII), containing the ethoxyethyl (EE) protecting group for one of its hydroxyls, was used as the starting compound. The silyl protection of the second hydroxyl and the liberation of the first with subsequent two-stage formation of the exo-methylene group

Scheme 20

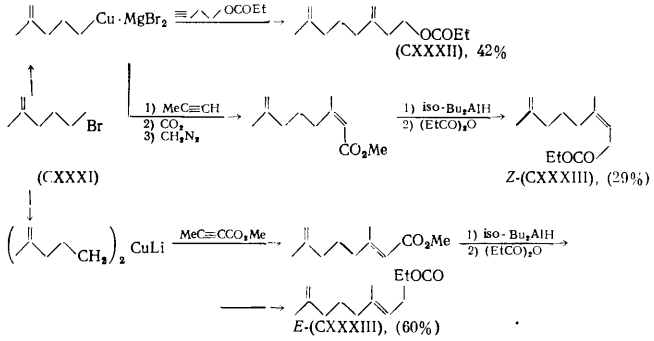


Scheme 21



led smoothly to the triene (CXXVIII). Its selective epoxidation at the activated C=C bond yielded the epoxyketone (CXXIX). A second epoxide ring was introduced into this molecule by Corey's method. The subsequent removal of the silyl protecting group and oxidation of the resulting alcohol led to the required compound (CXXX), which exhibited a high biological activity and whose physicochemical properties were found to be identical with those of the natural specimen. The use of various methods for the introduction of the epoxide ring and a change in the sequence of the operations indicated made it possible to obtain in addition two products, (CXXXa) and (CXXXb), isomeric with periplanone B, which differ in the configurations of the two epoxide units.

Scheme 22



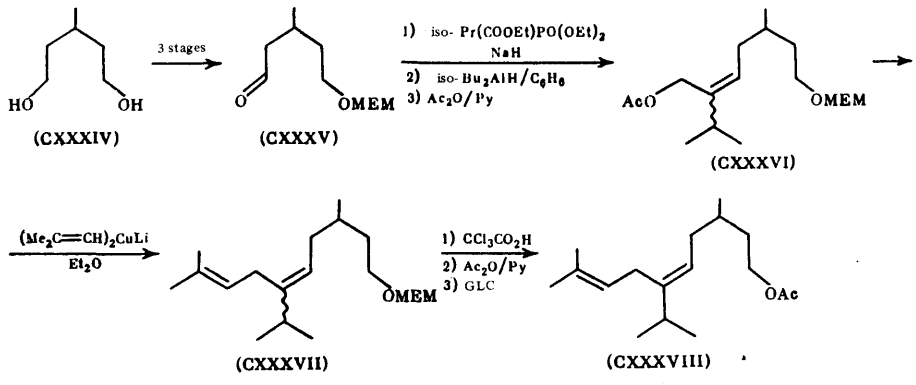
The SP of scale insects causing enormous damage, namely the yellow citrus scale insect *Aonidiella citrina* and the white plum scale insect *Pseudaulacaspic pentagona*, possess a more complex irregular sesquiterpene structure. The SP from the first of these insects, namely compound (CXXXVIII), has been obtained in an overall yield of 8% from the glycol (CXXXIV) in accordance with Scheme 23. This glycol was initially converted into the methoxyethoxymethyl (MEM) derivative of the aldehydoether (CXXXV). The conversion of the latter into the ethers (CXXXVI) and (CXXXVII) includes the Wittig–Horner addition of an olefin, which gives a mixture of isomers ($E/Z \cong 4:1$), and substitution of type $S_{N}2$ using lithium diisobutenyl cuprate. The required compound *E*-(CXXXVIII) was isolated in the last stage by means of preparative gas–liquid chromatography (GLC).[112]

9. The Pheromones of Scale Insects

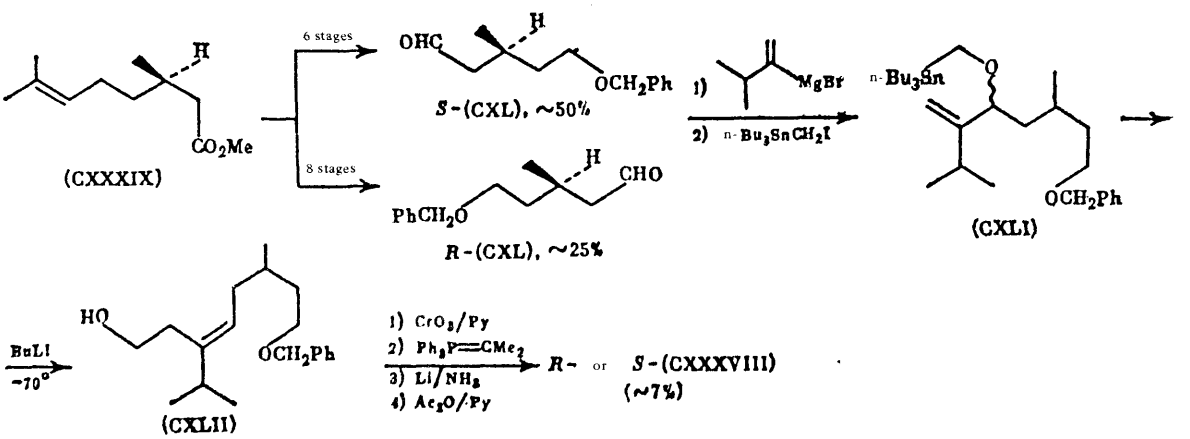
Much attention has been devoted recently to the study of the pheromones of certain scale insects. Thus, a widely distributed pest on various trees, including fruit trees, namely the San Jose scale insect *Quadraspidiotus perniciosus* produces a SP whose components are the propionates of α-myrcenol (CXXXII), α-nerol *Z*-(CXXXIII), and α-geraniol *E*-(CXXXIII).[108–110]

The key stage in the synthesis of each of the three components of this mixture is the addition of organocuprate derivatives of isohexenyl bromide (CXXXI) to substituted acetylenes (Scheme 22):[110,111]

Scheme 23



Scheme 24

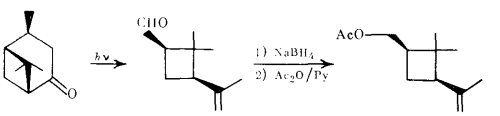


The chiral compounds (CXXXVIII), among which only the *S*-isomer proved to be biologically active, were synthesised (Scheme 24) from methyl *R*-(+)-citronellate (CXXIX) via the aldehydes *S*-(CXL) and *R*-(CXL). The conversion into the final compound (CXXXVIII) was achieved with the aid of the highly stereospecific 2,3-sigmatropic rearrangement of the stannanes (CXLI), leading to the *E*-isomers of compound (CXLII). The latter were converted into the (+)- and (-)-isomers of compound (CXXXVIII) in four fairly simple operations.[113]

Both enantiomers of the SP of the plum scale insect (CXLVI) were synthesised from the chiral aldehydes (CXLIII), which are readily available from the corresponding limonenes (Scheme 25).[114,115] The Corey–Yamamoto addition of an olefin to compound (CXLIII)[116] was first carried out using epoxyethane as the electrophile. The reaction apparently proceeds via the intermediate (CXLIV), giving rise to the trisubstituted homoallyl alcohols (CXLV) in a satisfactory yield and with exceptional stereospecificity (98% of the *Z*-isomer), the alcohol being subsequently converted into the required propionate (CXLVI). Comparison of the spectroscopic and biological properties of the synthetic and natural specimens showed that the latter has the 3*Z*, 6*R*-configuration.

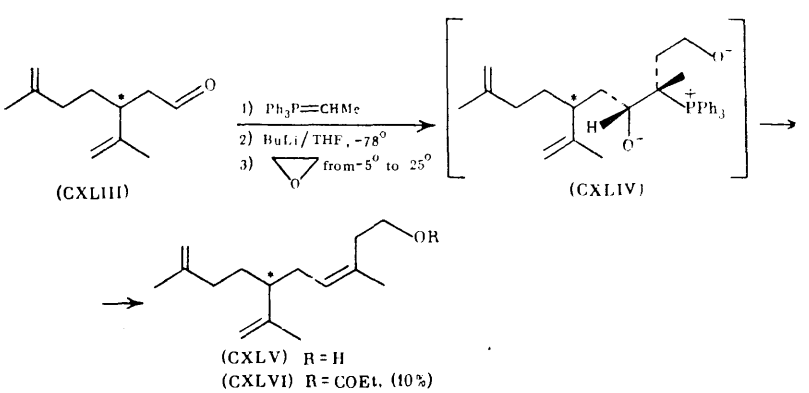
10. Other Sex Pheromones

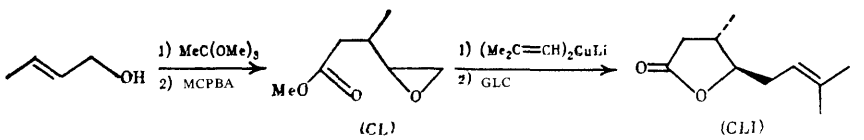
The citrus mealybug *Planococcus citri* is a citrus pest. Both enantiomers of its SP (CXLIX) have been recently synthesised by the photochemical cleavage of the corresponding *cis*-verbanones (CXLVII) (the yield was not indicated); the aldehydes formed in this process, for example, compound (CXLVIII), were then converted in two stages into the required acetates, among which the (+)-isomer (CXLIX) proved to be biologically active:[117]



The monoterpene lactone (CLI) has been identified as the SP of the pyralid Eldana saccharina—a sugar cane and maize pest. The synthesis of this compound, described without experimental details,[118] was achieved starting with crotyl alcohol via the epoxyester (CL); the required *trans*-isomer (CLI) was obtained by the addition of lithium di-isobutenyl cuprate:

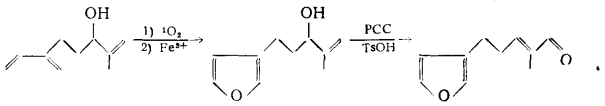
Scheme 25





(CL) (CLI)

Perillenal (CLII) is the SP of the pine sawfly *Neodiprion sertifer*, which causes significant damage to coniferous trees.[119] The pheromone (CLII) has been synthesised from the alcohol (XLVII), which can be obtained from myrcene (see above), by converting the 1,3-diene component of the molecule into a furan component and by oxidation with simultaneous allyl isomerisation of the alcoholic fragment:[67]



(XLVII) (CLII), 61% (CLII), 35%

It is noteworthy that compound (CLII) had been used earlier as an intermediate in the synthesis of perillene and dendrolasin (see Section IV, Scheme 32).

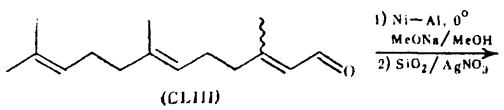
III. TRACK PHEROMONES AND TERRITORIAL MARKERS

Social insects widely employ chemical signals which determine the direction of the movement of separate individuals to the living quarters, a source of food, etc. Among substances controlling such behavioural responses, various linear and cyclic derivatives of the sesquiterpene and diterpene series have been discovered.

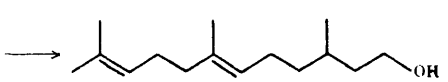
1. Terrestrol

S-(-)-2,3-Dihydrofarnesol (terrestrol) (CLIV) is produced by the males of the bumble bee *Bombus terrestris* and a number of other species of this family of insects[120–123] and is used by them as a marker on the route covered by their movements.

The simplest synthesis of compound (±)-(CLIV) consists in the reduction of *Z*/*E*-farnesal (CLIII) (readily available from dehydronerolidol) in the presence of the Ni–Al alloy and methanolic alkali:[124]

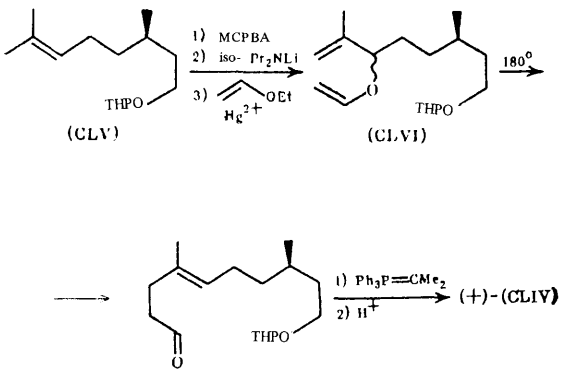


(CLIII)



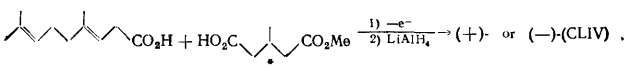
(CLIV), 61%

The synthesis of the optical isomers of compound (CLIV) has also been described. One of the syntheses is based on the ether (CLV) of *R*-(+)-citronellol, which is converted in the first three stages into a mixture of the diastereoisomers of the allyl vinyl ether (CLVI). Their subsequent Claisen rearrangement and combination with an olefin lead ultimately to *R*-(+)-(CLIV) in an overall yield of ~6%:[125]



(CLV) (CLVI)

In the second case both optical isomers have been obtained using homogeranic acid (CLVII) with the half-ester of D- or L-3-methylglutaric acid (CLVIII) in the key stage involving the Kolbe coelectrolysis:[126]



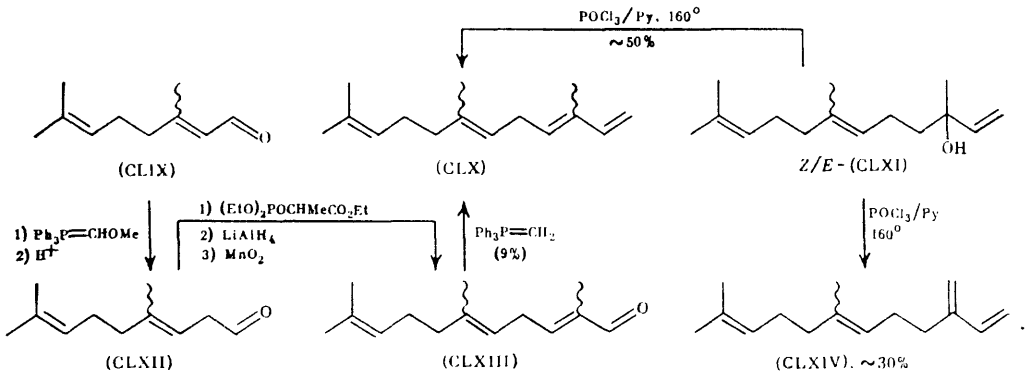
(CLVII) (CLVIII) ~(8%)

2. α-Farnesenes and Allofarnesenes

It has been shown recently that certain species of ants use various farnesene isomers, produced by the Dufur gland located in the rear part of the abdomen, as track pheromones and territorial markers. Thus *Z*,*E*-α-farnesene (CLX) has been detected in individual *Myrmica* species,[127] while the *E*,*E*-isomer of compound (CLX) [128] as well as *Z*,*Z*,*Z*-allofarnesene (CLXX) have been found in addition in the red ant *Solenopsis invicta*.[129,130]

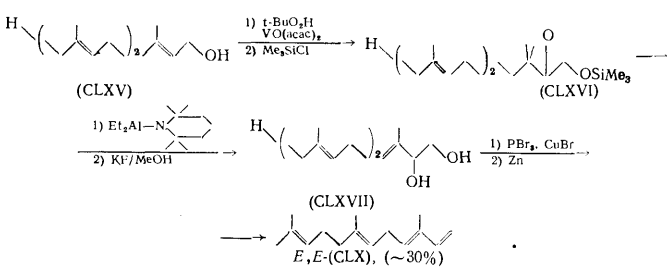
Some of these sesquiterpenes had been isolated still earlier from other natural sources and their synthesis, also giving rise to a series of possible regioisomers and stereoisomers, including β-farnesenes (CLXIV), has been achieved on the basis of citral (CLIX) and nerolidols (CLXI) (Scheme 26). The conversion of compound (CLIX) into the *Z*,*E*- and *E*,*E*-tetraenes (CLX) under consideration involves threefold combination with an olefin and the intermediate formation of the aldehydes (CLXII) and (CLXIII),[131] while vigorous dehydration of compound (CLXI) yields immediately all the isomers of the farnesenes (CLX) and (CLXIV) mentioned above.[128]

Scheme 26



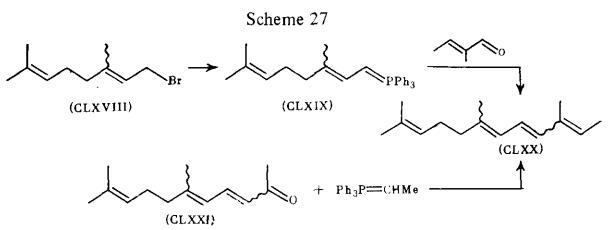
The low yields and the evident non-selectivity of the reactions considered above make it unlikely that the syntheses of α-farnesenes on the basis of the approaches described will be of much use.

The elegant synthesis of compound *E,E*-(CLX) from farnesol (CLXV), involving its selective epoxidation and rearrangement of the epoxide (CLXVI), is free from the above disadvantages. The diol (CLXVII) obtained in a high yield as a result was smoothly converted into the geometrically pure *E,E*-(CLX):[132]



Two approaches have been used (Scheme 27) in the syntheses of all the possible isomers of allofarnesene (CLXX), which made it possible to establish the configuration of the pheromone, which has the *Z,Z,Z*-geometry, as already mentioned.[130] The first synthesis involves the conversion of geranyl and neryl bromides (CLXVIII) into the corresponding phosphoranes (CLXIX) with subsequent addition of an olefinic group by these compounds to tiglic aldehyde, while the second synthesis involves an increase in the length of the isomeric pseudoionones (CLXXI) by a two-carbon fragment with the aid of ethylidenetriphenylphosphorane. It is difficult to estimate their effectiveness (the analysis has been carried out by GLC), but the simplicity of the chosen scheme is evident.

Scheme 27



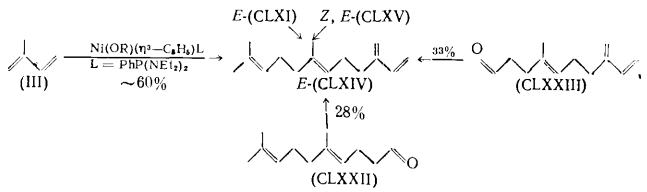
IV. FEAR PHEROMONES

Social insects widely employ chemical signals whose role reduces to warning of danger threatening members of the colony, which ultimately assists in the preservation of the species.

1. *E*-β-Farnesene

When attacked by a predator, many moth species instantly generate a mixture of substances with a protecting action and exhibiting simultaneously a repellant activity in relation to neighbouring members of the colony. The main component of this mixture is in many instances *E*-β-farnesene (CLXIV), which functions as a fear pheromone.[133–139] Special studies have shown that the *E*-geometry of the molecule of the given compound plays a decisive role in its function.[140,141]

The simplest pathway to compound *E*-(CLXIV) consists in the Ni(0)-catalysed trimerisation of isoprene.[142,143] Among other methods, mention should be made of the dehydration of nerolidol *E*-(CLXI)[128] and the six-stage transformation of farnesol *Z,E*-(CLXV),[132] which has been carried out in full conformity with the schemes for the synthesis of α-farnesenes discussed above. Finally, the synthesis of *E*-(CLXIV) from the relatively readily available C_{12}-aldehydes (CLXXII)[48,144] and (CLXXIII)[145] by standard procedures, involving the lengthening of the isoprenoid chain by a three-carbon fragment, has been described:

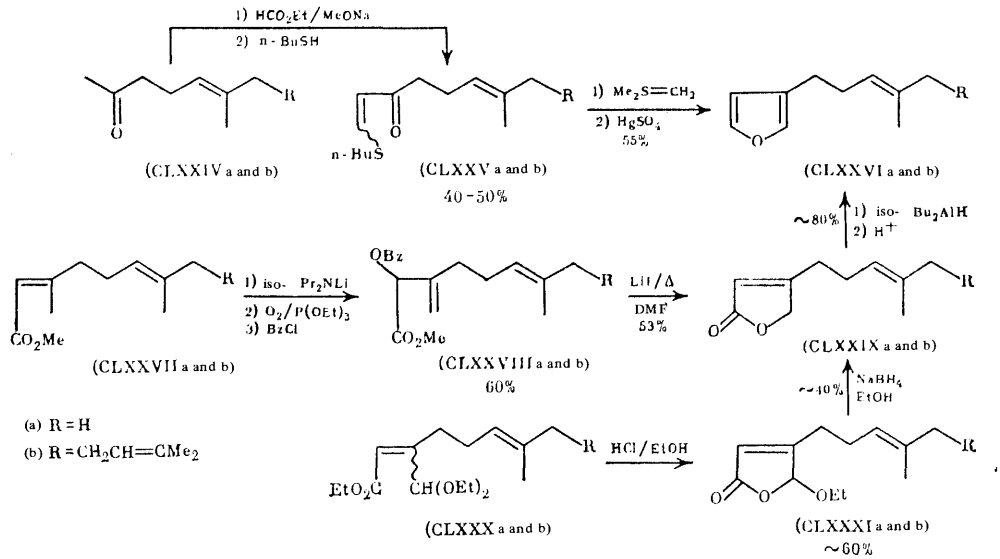


2. Perillene and Dendrolasin

Certain ant species produce perillene (CLXXVIa) and dendrolasin (CLXXVIb) as fear pheromones; these furanoterpenes can in addition fulfil protecting functions.[146,147]

A whole series of syntheses of both pheromones have now been described. One group of syntheses is based on the construction of a 3-substituted furan ring, while those in another begin with furan derivatives already synthesised

Scheme 28

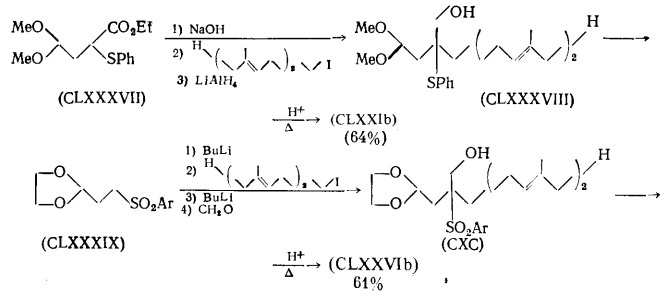


having a functional group at C(3). Thus formylation of methylheptanone (CLXXIVa) or geranylacetone (CLXXIVb) in accordance with Scheme 28 and the interaction of the corresponding thiovinyl ketones (CLXXV, a and b) with dimethylsulphonium methylide yield, after intramolecular cyclisation of the intermediate epoxides and the cleavage of the C–S bond, the required furanoterpenes (CLXXVI, a and b) in an overall yield of ~25%.[148] The conversion of the monoterpene esters (CLXXVIIa) and (CLXXXa) and the sesquiterpene esters (CLXXVIIb) and (CLXXXb) into the same products reduces to the formation of the corresponding furanones (CLXXIX, a and b) and includes the formation of the intermediate allyl benzoates (CLXXVIII, a and b) [149] or the hemiacetals (CLXXXI, a and b).[150] The conversion into the furans (CLXXVI) is carried out almost quantitatively by the acid treatment of the lactols arising on mild hydride reduction of the furanones (CLXXIX).

Other methods of synthesis of compound (CLXXVI) are presented in Scheme 29. According to one of them,[151] the aldehyde (CLXXXIII) is made to combine with an olefinic fragment by means of the phosphorane (CLXXXII), which is readily obtainable from maleic anhydride, to form the half-ester (CLXXXIV), which is transformed as a result of three simple operations into compound (CLXXIXa). In another method the condensation of the chlorozinc derivative (CLXXXVI) with the bromofuranone (CLXXXV), catalysed by a palladium complex, yields the required product (CLXXIXb) in a single stage.[152] Despite the evident effectiveness of both methods, the limited availability of the initial aldehyde (CLXXXIII) and the bromo-derivative (CLXXXV) must be emphasised.

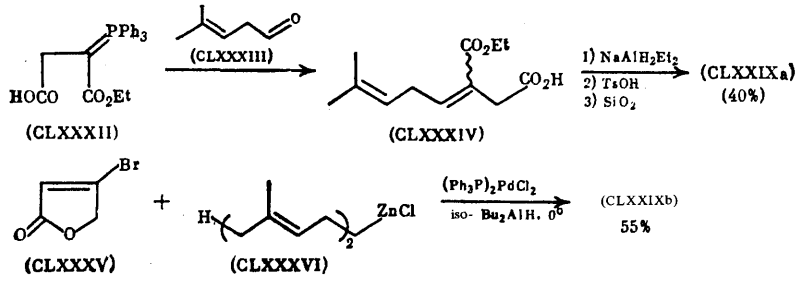
An approach to the synthesis of dendrolasin (CLXXVIb) based on the sulphur-containing acetals (CLXXXVII) and (CLXXXIX) (Scheme 30) is of definite interest. Their deprotonation and subsequent alkylation by homogeranyl iodide followed by the reduction of the ester group or condensation with formaldehyde lead to the corresponding primary alcohols (CLXXXVIII) and (CXC) in high yields. These alcohols are readily converted into the required product (CLXXVIb) by refluxing with toluene-*p*-sulphonic acid in benzene.[153]

Scheme 30



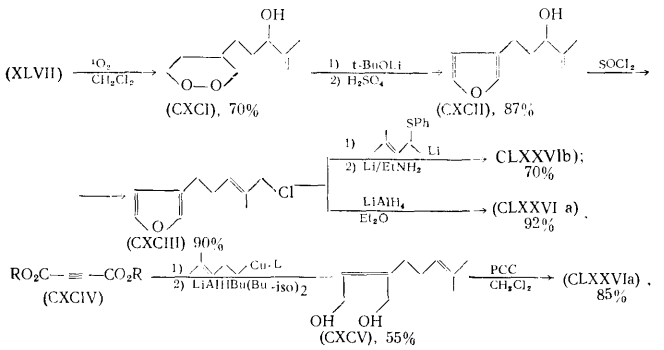
Among other methods for the formation of the hetero-aromatic ring of the pheromones (CLXXVI) based on linear precursors, mention must be made of those based on the photochemical oxidation of the 1,3-diene component of the alcohol (XLVII), which leads to the peroxide (CXCI),[66] and

Scheme 29



on the synthesis of the glycol (CXCV) from acetylenedicarboxylic ester (CXCIV) [154] (Scheme 31). The isomerisation of compound (CXCI) on treatment with a strong base and dehydration of the intermediate lactol afford the furan carbinol (CXCII) which is then converted into the allyl chloride (CXCIII). Its hydrogenolysis or the addition of a C_5 unit to it lead ultimately to compound (CLXXVIa) or (CLXXVIb) respectively. Perillene (CLXXVIa) has been obtained almost quantitatively in a single stage by oxidising the glycol (CXCV) with PCC.

Scheme 31

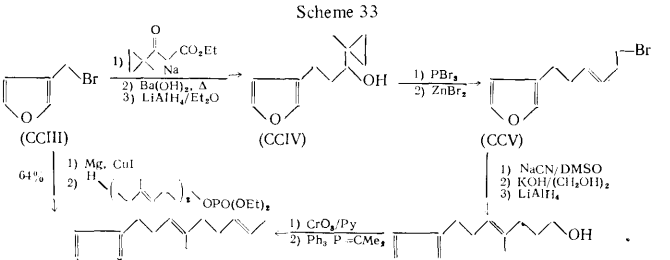


As already mentioned, the syntheses of compound (CLXXVI) in the second group begin with the furan C_5-synthones and reduce to the formation of the isoprenoid side chain. Scheme 32 illustrates one of the approaches using β-furylmethanol (CXCVII) with a Claisen type rearrangement as the key stage. Thus thermolysis of the vinyl ester (CXVI) gave a moderate yield of perillenal in the form of a mixture with $E/Z \cong 5:1$. Repetition of the above operations using the allyl alcohols (CXCIX) ($E/Z \cong 2:1$) led to the aldehyde (CCI) and both products, (CLII) and (CCI), were converted in accordance with the same scheme into the corresponding furanoterpenes (CLXXVI),[155] whose overall yields cannot be estimated. In another version[156] the alcohol (CXCVII) was converted into the aldehyde (CXCVIII) by increasing the length of the chain by a two-carbon fragment in a five-stage process. The aldehyde gave rise to the vinyl ether (CC) in two stages and thermolysis of the ether resulted in the formation of the aldehyde (CCII). The addition of an olefinic fragment to compounds (CXCVIII) and (CCII) by the Wittig method yields the required products (CLXXVIa) and (CLXXVIb) respectively.

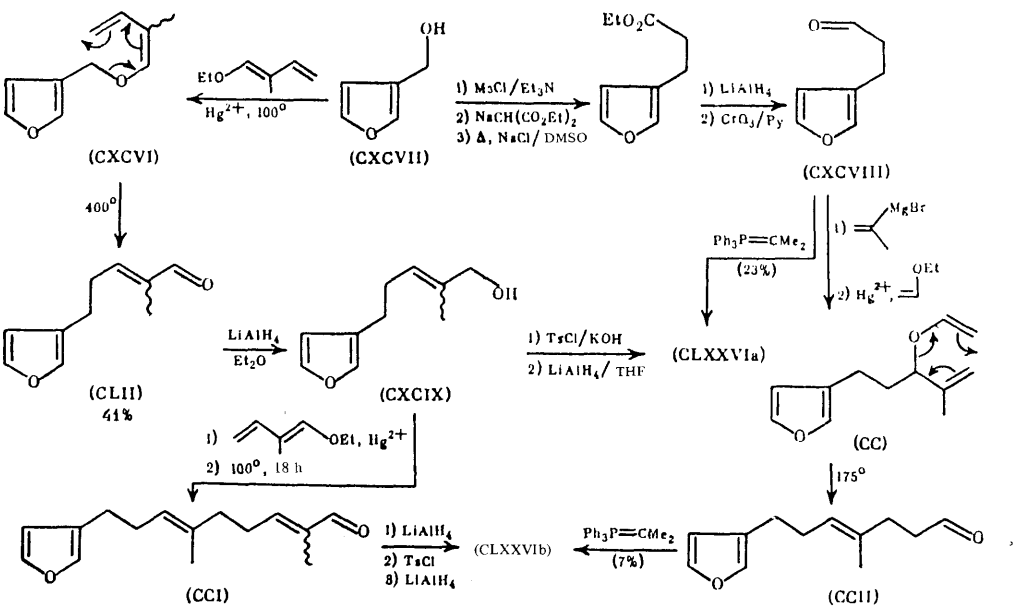
One of the first syntheses of dendrolasin (Scheme 33) is based on the conversion of the bromo-derivative (CCIII) into the cyclopropylcarbinol (CCIV). Its homoallyl rearrangement proceeds stereospecifically, giving rise to the bromo-derivative (CCV). The increase of the side chain of the latter by one carbon atom with formation of the alcohol (CCVI) as well as the conversion of the latter into compound (CLXXVIb) were achieved by standard methods, but the yields of the products in the overall scheme were not indicated in the study under discussion.[157]

The single-stage pathway to compound (CLXXVIb), starting with the same bromo-derivative (CCIII) and consisting in the CuI-catalysed condensation of the latter in the form of a Grignard reagent with geranyl diethyl phosphate, appears to be more effective.[158] The allyl regioisomer is formed simultaneously in 17% yield and is separated chromatographically from compound (CLXXVIb).

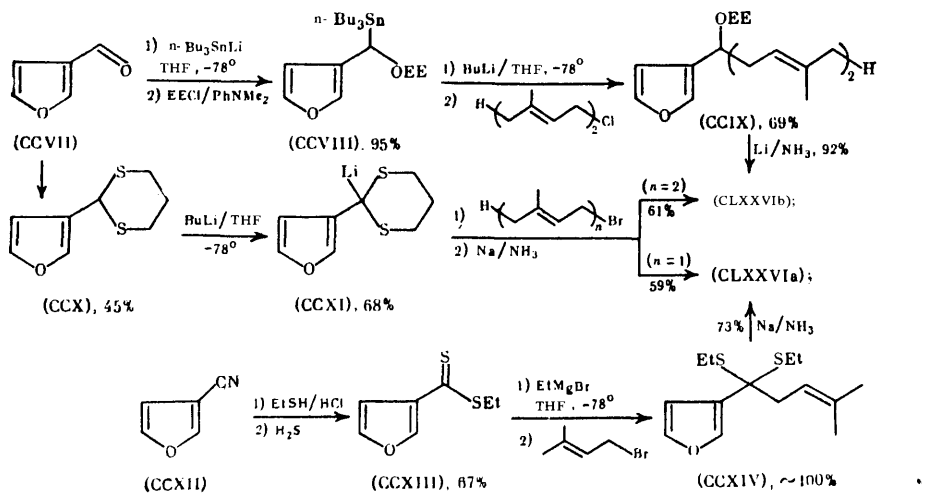
Scheme 33



Scheme 32



Scheme 34



A large group of syntheses of the pheromones (CLXXVI) begin with β-formylfuran (CCVII) and β-cyanofuran (CCXII) (Scheme 34). Thus stannylation of compound (CCVII) gives rise to a carbinol, which has been isolated in the form of the ethoxyethyl ether (CCVIII). Its metallation and alkylation lead to the derivative (CCIX), whose hydrogenolysis gives rise to dendrolasin in an overall yield of 60%.[159] The syntheses of compounds (CLXXVI) by the alkylation of the lithio-derivative (CCXI), the dithioacetal (CCX),[160] and the related magnesio-derivative, formed *in situ* on interaction of the thioether (CCXIII) with an excess of ethylmagnesium bromide,[161] proved to be just as effective. The reductive cleavage of the intermediate dithioacetals of the type (CCXIV) has been achieved in both cases without complications on treatment with sodium in liquid ammonia.

In conclusion, it must be emphasised that the present review covers data on the synthesis of only monoterpene and sesquiterpene pheromones. The methods of synthesis of certain linear and macrocyclic diterpenoids, identified as pheromones in various insect species, have not been included.

The data examined thus illustrate the abundance of the synthetic procedures, both traditional and most modern, which are used to construct the molecules of a wide variety of isoprenoid pheromones. In the immediate future one may expect a further improvement of such procedures as a result of the elucidation of the structures of new compounds and also in view of the constantly growing need for the synthesis of low-molecular-weight bioregulators belonging to this important class.

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During the preparation of the manuscript for the press, a number of publications concerning its individual sections have appeared. Thus the racemic ipsenol and ipsdienol have been obtained recently in high yields by the condensation of two C_5 fragments—of the silane (IX) with isovaleraldehyde and dimethylacrylic aldehyde respectively in the presence of Bu_4NF [162] or with the chlorides of isovaleric and dimethacrylic acids in the presence of $TiCl_4$.[163] The synthesis of the above pheromones as a result of the reaction of the bromo-derivative (IV), catalysed by the Zn/Ag couple, with the nitriles of the above acids is also effective.[164] The Kondakov acylation of isoprene by the chloride of dimethylacrylic acid using $EtAlCl_2$ as the catalyst affords, after the reduction of the intermediate ketone, ipsdienol in 12% yield.[165] Two extremely effective syntheses of compound (XXXII) from myrcene have also been published. In one case myrcene is epoxidised at the trisubstituted C=C bond with subsequent isomerisation of the epoxide on treatment with MeMgI,[166] while in the other case it is converted by a standard method[67] into amitinol, whose acetate isomerises on treatment with $HClO_4$.[167] Both enantiomers of compound (XXXII) were obtained in this process by the chiral reduction of ipsdienone, albeit in a low optical yield.[167]

The key stage in the six-stage syntheses of racemic derivatives of grandisol and lineatin has been the intramolecular cyclisation of 4-bromo-1-trimethylsilylbutyne[168] and 2,5,5-trimethylocta-1,6,7-trien-4-ol [169] respectively. The details of the synthesis of the racemic compound (XCVI) considered in Scheme 20 [101] and of both its enantiomers have been published recently.[170]

The pheromone (CXCIX) of the citrus mealybug has been synthesised non-stereospecifically by adding organocuprates to sulphonylbicyclobutanes.[171] On the other hand, two procedures for the preparation of eldanolide (CLI) from *S*-(+)-glutamic acid and the methyl ester of *R*-(+)-citronellic acid[173] respectively, which have made it possible to establish the 3*S*, 4*R*-configuration of the natural product, are characterised by a high enantioselectivity. Perillenal has been obtained by the allyl oxidation of perillene by SeO_2 in 42% yield.[174]

Farnesene *E*-(CLXIV) has been synthesised recently by the photolysis of 6*E*-farnesyl iodide in 80% yield;[175] the synthesis of this tetraene by the $ZnCl_2$-catalysed condensation of geranyl bromide *E*-(CLXVIII) with isoprenylstannane has been somewhat less successful.[176]

The key stage in the synthesis of perillene (yield not indicated) has been the radical cyclisation of a derivative of γ-dimethylallylpropargyl alcohol.[177] A further three approaches to β-prenylfurans (CLXXVI) from β-substituted furan C_5-synthones have also been published. Thus the reaction of the tosylate obtained from the alcohol (CXCVII) with lithium diprenyl cuprate[178] or of the bromo-derivative (CCIII) with a C_5 π-allylnickel complex[174] gives rise to perillene in 15% yield. On the other hand, a high yield of this compound as well as dendrolasin has been achieved by the Grignard reaction of the same bromo-derivative

(CCIII) with prenyl and geranyl diethyl phosphates respectively.[179]

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Zelinskii Institute of Organic Chemistry,
USSR Academy of Sciences, Moscow

Translated from *Uspekhi Khimii*, 53, 1740-1763 (1984) U.D.C. 543.544.4:577.150

Affinity Adsorbents Based on Carriers Activated by Epoxy-compounds

B.A.Klyashchitskii and P.V.Kuznetsov

The review is devoted to the synthesis and applications of affinity adsorbents based on carriers activated by epoxy-compounds. The methods for the introduction of epoxy-groups into carriers of different chemical types are discussed and conditions for the immobilisation of three-dimensional spacers and low-molecular-weight and polymeric ligands on carriers containing epoxy-groups are considered. Data are presented on the properties and applications of adsorbents of this type in affinity chromatography.
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I. INTRODUCTION

Extensive data have now accumulated on the synthesis and practical applications in affinity chromatography (AFC) of various types of adsorbents, which have been described systematically in a series of monographs[1-4] and reviews.[5-11] Reviews devoted to specific problems arising in the biospecific purification of individual classes and groups of biopolymers have appeared recently.[12-14]

The development of AFC would have been impossible without continual improvement of the chemical basis of this method, which includes the methods of synthesis and activation of solid carriers, the immobilisation of ligands, the analysis of affinity adsorbents, the study of their properties, etc. The chemical aspects of the AFC method have been the subject of discussion in the above monographs, individual reviews,[15,16] and conferences devoted to AFC.[17] A review of the synthesis and properties of adsorbents for covalent chromatography has been published.[18] It has apparently now become necessary to give a systematic account of specific chemical data on the methods of synthesis of affinity adsorbents of different types. The present review is devoted to the synthesis, properties, and applications of biospecific adsorbents of one of the most promising types, namely adsorbents based on epoxy-activated carriers (EAC).

Data on the affinity adsorbents based on EAC have been described in the literature extremely sketchily and in a fragmentary fashion. Nevertheless the application of adsorbents of this kind is organically linked to an urgent problem in AFC—the synthesis of stable materials resistant to hydrolysis, exhibiting a high biospecificity, and capable of functioning for a long time under various conditions. The employment of the classical method of the bromocyanogen activation of polysaccharide carriers[19] does not allow the preparation of adsorbents with a bond between the matrix and the spacer† (ligand) which is highly resistant to hydrolysis.[10-20] Despite a number of successful studies[21-24] using the polymeric spacers in accordance with the principle of multipoint addition, the attention of investigators has been attracted with increasing frequency by adsorbents based on EAC, including Sepharoses.

Apart from a high resistance to hydrolysis, the EAC possess a number of other important advantages—they are fairly hydrophilic and virtually lack charged groups, which reduces to a minimum the non-specific interactions between the biopolymer isolated and the adsorbent. These adsorbents make it possible to immobilise not only ligands with a primary amino-group but also (without additional modification) ligands with other functional groups, for example hydroxy-, carboxy-, and thiol groups. When EAC are used, it is frequently not necessary to introduce additional spacers. It is also quite important that, in the epoxy-activation of agarose carriers, a cross-link is formed between the agarose chains themselves, which imparts additional rigidity to adsorbents of the type of Sepharose and increases the mechanical and chemical stability of the carrier.

The present review gives a systematic account of the principal literature data on the synthesis and applications of adsorbents based on EAC for the purpose of AFC and also for the immobilisation of enzymes.

II. METHODS FOR THE ACTIVATION OF SOLID CARRIERS BY EPOXY-COMPOUNDS

The activation of solid carriers by epoxy-compounds was first proposed in the laboratory of Porath,[25-28] who has made a major contribution to the development of the methods for the separation of biopolymers in general and of AFC in particular.[29]

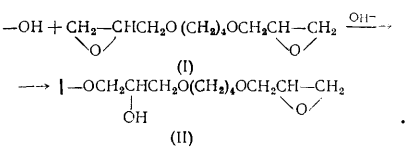
Sepharoses of various brands (2B, 4B, 6B, and CL), satisfying the majority of the requirements which must be met by carriers for the preparation of affinity adsorbents, are used most frequently in activation by epoxides and their derivatives. Celluloses, ultragel, Sephadexes, and other polysaccharide carriers are used more rarely. The employment of methacrylate, methacrylamide, and hydroxylalkyl methacrylate polymeric carriers,[30-33] as well as silica carriers[33,34] has been described.

†The term "spacer" used in the present review [the term "vstavka" or "insert" [10] was employed in the original Russian text (Ed.of Translation)] denotes a compound (or group of atoms) separating the ligand from the surface of the solid carrier. The terms "arms" and "leash" can also be encountered. Apart from "vstavka" mentioned above, the terms "prostranstvennaya gruppa" ("space group"), "speiser" (spacer), and "nozhka" (foot) are also used in the Russian scientific literature.

1. Activation of Polysaccharide Carriers

The methods for the activation of polysaccharide carriers by epoxy-compounds can be divided arbitrarily into two main groups: methods leading to the appearance of highly reactive terminal epoxy-groups on the surface of the carrier [the Sundberg–Porath method (1974) [27] and the method of Axen and co-workers (1975) [35]] and also methods making it possible to modify the surface of the carrier by various functional groups [Hjerten's method (1974) [36,37]].

(a) *The Sundberg–Porath method.* The method is based on the reaction of bisoxirans of the type of diglycidyl ether of butane-1,4-diol (I) with Sepharose in a highly alkaline medium (0.4–0.6 M sodium hydroxide)#:

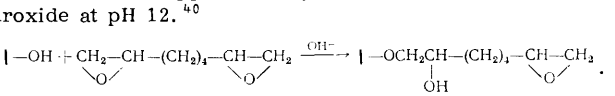


(I) (II)

The reaction time is 6–10 h and the temperature is 20 to 30 °C. The optimum concentration of the bisorixan (I) in the reaction mixture is approximately 30%.[27] The concentration of the epoxy-groups on adsorbent (II) was approximately 800 μmole per gram of the dry gel. According to the data of Sundberg and Porath, the stability of epoxy-activated gels is a maximum when they are stored in dimethyl sulphoxide at 4 °C or in 1 M sodium chloride at pH 6.8 and 4 °C. The epoxidation of CL-Sepharose by this method made it possible to employ the activated matrix for syntheses in non-aqueous media.[38]

The use of the bisoxiran (I) for the activation of cellulose has been recently reported.[39] The activation takes place in 0.6 M sodium hydroxide with added sodium tetrahydroborate (4 mg ml^{-1}) at approximately 20 °C for 18 h. The activity of epoxy-cellulose was fully retained for two weeks when it was stored in 0.1 M sodium hydroxide at 4 °C.

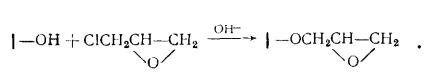
1,2:7,8-Diepoxyoctane (III) has also been used as the reagent for the activation of alginic acid. The epoxidation was carried out at approximately 20 °C for 3 h in 5 M sodium hydroxide at pH 12.[40]



(III)

The Sundberg–Porath method constitutes the basis of the synthesis of the commercial preparation "epoxy-activated Sepharose 6B" (EAS-6B) manufactured by Pharmacia Fine Chemicals (Sweden).

(b) *The Axen method.* This method of activation was first proposed to synthesise (via epoxy-derivatives) highly substituted thiol-containing gels for covalent chromatography.[35] The epoxidation of Sepharose by epichlorohydrin (1-chloro-2,3-epoxypropane) (IV) takes place fairly readily at 60 °C in the course of several hours in 1 M sodium hydroxide:



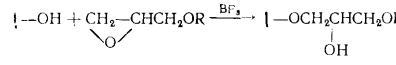
(IV) (V)

When 0.45 ml of compound (IV) was used for 3 g of the gel, the degree of substitution of approximately 600–700 μmoles of epoxy-groups per gram of dry gel (V) was attained. The optimisation of the epoxidation reaction conditions was subsequently investigated[41] and the following activation conditions were proposed: 30% of Sepharose, 5% of epichlorohydrin, and 0.4 M sodium hydroxide (2 h, 40 °C). It is of interest to note that the attempt to employ added organic solvents in the epoxidation reaction (25% solution of dimethyl sulphoxide or dioxan) did not increase appreciably the amount of epoxy-groups introduced. However, it was shown that in 25% dimethyl sulphoxide a degree of substitution of approximately 700 μmoles of epoxy-group per gram of the dry gel is attained after approximately 1 h, although the highest degree of substitution (800 μmole g^{-1}) is observed when the reaction is carried out in an aqueous medium for 2 h at 40 °C.

Other modifications of the method of Axen and co-workers have also been described. Thus Sepharose (IV) has been epoxidised with 0.48 M epichlorohydrin in 0.5 M sodium hydroxide at 30 °C in the course of 4 h.[42] According to other data,[43] the use of a solution of cetyltrimethylammonium bromide in the epoxidation reaction increased the quality of the gel and made it possible to reduce the activation time to 45 min at 45–50 °C. A method has been described recently[44] for the activation of Sepharose in 2 M sodium hydroxide with the gradual addition of epichlorohydrin to the reaction mixture over a period of 8–10 h at approximately 20 °C. The authors do not quote data for the degree of substitution of the gel by epoxy-groups, although the subsequent immobilisation of a number of enzymes (malate dehydrogenase, lactate dehydrogenase, and alkaline phosphatase) on the metal chelate carriers obtained was successful.

At the present time the method of Axen and co-workers is used to epoxidise Sepharose in order to obtain the commercial preparation "Thiopropylsepharose 6B" (Pharmacia Fine Chemicals). In addition activation of ultragel of type A4R with the aid of compound (IV) constitutes the basis of the preparation of commerical affinity adsorbents produced by the LKB Company (Sweden)—"acriflavin–A4R ultragel" and "heparin–A4R ultragel".

(c) *The Hjerten method.* This method was first developed by the authors in 1974 for the synthesis of neutral gels widely used in hydrophobic chromatography.[36,37] It is based on the reaction of Sepharose with a wide variety of epoxy-compounds in the presence of a catalyst—boron trifluoride:



A large number of hydrophobic adsorbents containing in their structure terminal alkyl and aryl groups, including those with alcoholic, carboxy-, methoxy-, cyano-, and other substituents, have been synthesised by this method.[45,46] The Sepharose gel:dioxan volume ratio in the reaction is 1:1; 1 ml of boron trifluoride etherate is used for 100 ml of the gel suspension. When 5 min have elapsed after mixing the reactants, the corresponding glycidyl ether is added and the reaction mixture is stirred for 40 min at 25 °C. The concentration of the ligands on adsorbents of this type was determined by NMR after acid hydrolysis. The capacity of the adsorbents with respect to the ligand reached 200 μmoles per gram of the dry gel.

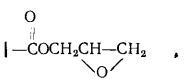
The method of Hjerten and co-workers is the basis of the preparation of the widely used stable hydrophobic commercial adsorbents "octyl-Sepharose CL-4B" and "phenyl-Sepharose CL-4B" (Pharmacia Fine Chemicals) whose capacity in relation

#Here and henceforth the bold line in the reaction schemes denotes the surface of the solid carrier.

to the binding of protein (serum albumin) reaches 15–20 mg per ml of the gel.

2. Synthetic Polymeric Carriers containing Epoxy-Groups

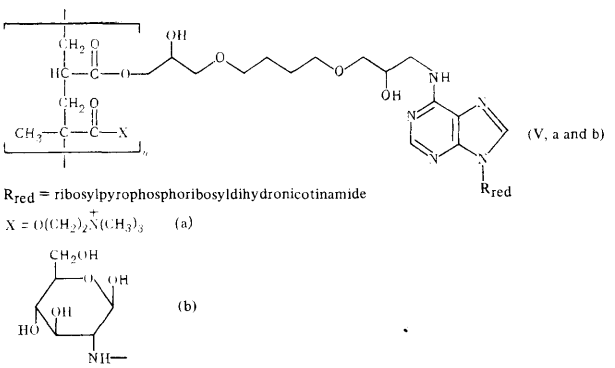
In the group of insoluble matrices obtained synthetically, glycidyl methacrylate gels (GMG), first synthesised by Czechoslovak investigators for the radical copolymerisation of ethylene methacrylate and glycidyl methacrylate, are of considerable interest.[32,33,47] The capacity of the carriers obtained with respect to the epoxy-groups was about 3.5 mmol g^{-1} and the epoxy-group was located on the surface of the carrier on a three-atom spacer:[47]



Turkova et al.[48] recently obtained hydroxyalkyl methacrylate gels (Separons H 300 and H 1000), activated by the epichlorohydrin, and, depending on the degree of activation, the content of the epoxy-groups was 140–1770 μmoles per gram of dry weight. It is of interest to note that the removal of the unreacted epoxy-group after the addition of the ligand, usually achieved by condensation with ethanolamine, was carried out by hydrolysis with 0.1 M perchloric acid.

Another example of EAC based on glycidyl methacrylate is provided by the "oxiran-acrylic carriers" manufactured by Pöhm Pharm (Federal Republic of Germany).[31] It is known that the second component in the copolymerisation reaction is allyl glycidyl ether, methacrylamide, or methylenebisacrylamide. The carriers obtained have a macroporous structure, contain a large number of epoxy-groups (800 to 1000 μmoles per gram of the dry carrier), their swellability does not vary over a wide pH range (from 1 to 10), they have a high mechanical and hydrolytic stability, and they are resistant to microbes. The successful application of the oxiran-acrylic carriers to the immobilisation of proteins and enzymes has been demonstrated.[31] For example, the amount of bound albumin reached 140 mg and that of trypsin was equivalent to 600 activity units per gram of dry carrier. This type of carrier is apparently promising for employment in AFC.

The synthesis of two water-soluble polymers on which NADH was subsequently immobilised, has been described.[30] The first was a copolymer of methacryloylcholine and 3-[4-(2,3-epoxypropoxy)butoxy]-2-hydroxypropyl acrylate. The immobilisation of NADH on this copolymer was achieved in three stages: alkylation of NAD at the N(1) atom, reduction of the nicotinamide component with dithionite, and Dimroth rearrangement involving the transfer of the alkyl bond from the N(1) atom to the exocyclic amino-group of the adenine component. The second polymer was a copolymer of the same epoxy-monomer and *N*-methacryloyl-2-glucosamine. NADH was added to this copolymer via the amino-group at the C(6) atom in a single stage. This resulted in the formation of the conjugates (V, a and b):



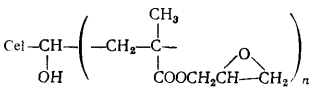
R_{red} = ribosylpyrophosphoribosyldihydronicotinamide

X = $O(CH_2)_2\overset{+}{N}(CH_3)_3$ (a)

(b)

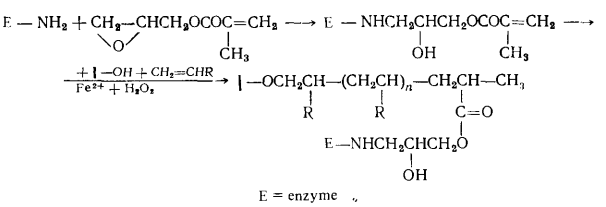
(V, a and b)

The copolymers of cellulose and poly(glycidyl methacrylate) having the following structure have also been obtained:



Cel = cellulose

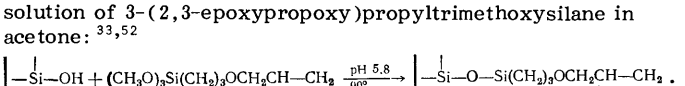
They have also been used to prepare immunosorbents[49] and for the immobilisation of certain enzymes.[50] A new type of polymeric material, consisting of a hydrophilic polysaccharide component and a synthetic hydrophobic polymer, has been obtained by graft polymerisation.[51] Sepharose 4B and the Sephadexes G-10 and G-200 were used as the polysaccharide matrices. The copolymerisation process with immobilisation of enzymes (α-amylase, chymotrypsin, and others) can be represented schematically as follows:



E = enzyme

3. Activation of Silica Carriers by Epoxy-Compounds

The activation of carriers of this type has been inadequately investigated, although macroporous silica carriers are in fact important for the introduction of the AFC method into technological schemes for the purification of biopolymers. Porous glasses have been activated by treatment with a 5% solution of 3-(2,3-epoxypropoxy)propyltrimethoxysilane in acetone:[33,52]



A number of enzymes have been successfully immobilised on the carrier obtained and the capacity with respect to the protein was in the range 10–80 mg of the protein per gram of the carrier.[33] The same reagent in the form of a solution in toluene has been used to introduce the epoxy-groups into the silica carrier silochrome.[34] The activation of the "Fractosil-1000" (Merck) silica has been carried out analogously. The capacity of the resulting carrier with

respect to the protein was 20–30 mg per gram of the carrier.[33]

III. IMMOBILISATION OF LIGANDS ON CARRIERS CONTAINING EPOXY-GROUPS

One of the significant advantages of the EAC based on Sepharose (EAS-6B) is the absence of a special stage involving the introduction of a spacer in the synthesis of the affinity adsorbent. Indeed EAS-6B, obtained by the Sundberg–Porath method, has a fairly long hydrophilic spacer which permits the immediate immobilisation of the ligand. This simplifies the syntheses of adsorbents with low-molecular-weight ligands to the maximum extent and in a number of instances results in a process consisting of only one stage.

On the other hand, the application of activated Sepharose, obtained by the method of Axen and co-workers (1,2-EPS), as a rule requires the introduction of an additional spacer. The ligand immobilisation reactions will be considered below in relation to the above types of epoxy-Sepharose.

1. Adsorption of Low-Molecular-Weight Ligands or Spacers

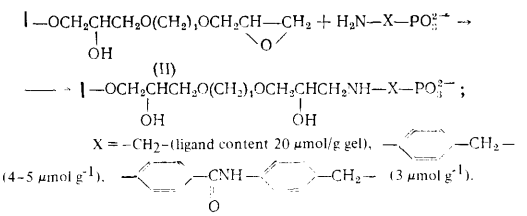
(a) *Adsorbents based on EAS-6B.* As a rule the immobilisation of ligands containing amino-, hydroxy-, or mercapto-groups takes place readily at pH from 7 to 13 at a temperature of 20–45 °C in the course of 10–65 h. These general conclusions are illustrated by specific examples in Table 1.

Table 1. Conditions for the immobilisation of low-molecular-weight ligands with amino-, hydroxy-, and mercapto-groups on EAS-6B.

Ligand	pH	Temperature, °C	Time, h	Refs.
		NH_2		
Trimethoprim analogue	9–10	—	16	[53]
Folic acid	10	30	16	[54]
8-Aminoxanthene	10–11	37	20	[55]
Acriflavin	11.5	20	8–10	[56]
S-Hexylglutathione	12	30	16	[57]
Galactosamine	13	30	20	[58]
		OH		
Ribose-5-phosphate	8.5	33	65	[59]
N-Acetylgalactosamine	11	40	16	[60]
Adenosine	11.2	37	24	[61]
Glycerylphosphorylcholine	13	45	20	[62]
		SH		
Reduced glutathione	7*	37	24	[63]

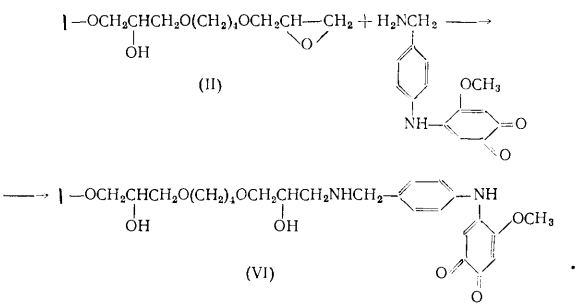
*The immobilisation was carried out in an atmosphere of nitrogen.

Under analogous conditions (0.1 M sodium hydroxide at pH 13), aminomethylphosphonic acid and derivatives of *p*-aminobenzylphosphonic acid were coupled to EAS-6B and the capacity of the adsorbent with the ligand containing the aliphatic amino-group proved to be approximately 4–5 times higher:[64]



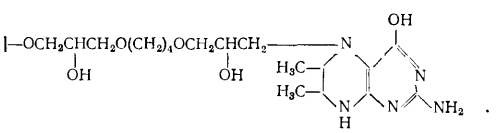
It is of interest that only adsorbents with an aromatic structure were capable of weak binding of alkaline phosphatase.

The use of amino-derivatives of 1,2-benzoquinone as ligands has been described.[65] The reaction was carried out at pH 10 in 0.07 M carbonate buffer solutions in a stream of nitrogen in the course of 5 h; the resulting capacity with respect to the ligand was entirely satisfactory—5.5 μmoles per ml of the packed volume of the gel:



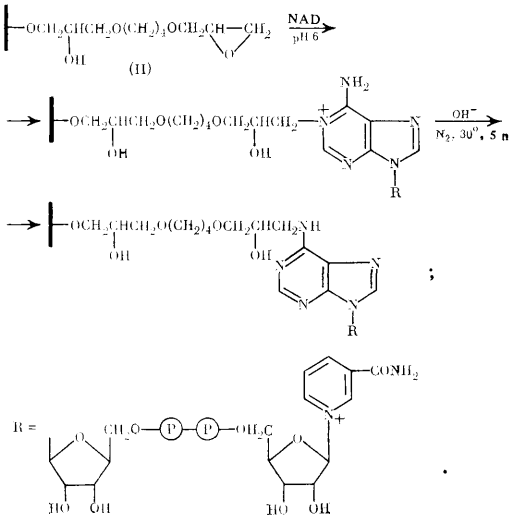
The adsorbent (VI) synthesised proved to be highly stable and was used for about a year for the isolation of menadione reductase.

A high capacity with respect to the ligand—approximately 280 μmoles per gram of gel—has been obtained following the immobilisation via the 5-position of the dimethyl derivative of 2-amino-4-hydroxytetrahydropteridine.[66] The reaction was carried out in deaerated 0.5 M sodium carbonate solution at pH 11.4:



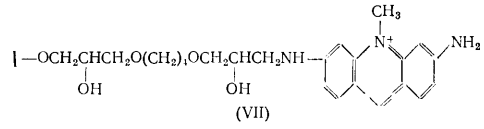
When the ligand contains carboxy-groups, it can be immobilised on the adsorbent as a result of the formation of ester linkages.[33,67] Ligand containing a phenolic hydroxyl also add effectively to EAS-6B in an acid medium. However, when the ligand contains both functional groups, the exact binding sites cannot be always established. Thus the exact structure of the adsorbents obtained from derivatives of auxin (5-hydroxyindolylacetic acid, 2-, 3-, and 4-hydroxyphenylacetic acids, etc.) and antiauxin (2-hydroxy-3,5-diiodobenzoic acid).[68] According to the authors, the adsorbents with indolylacetic acid as the ligand proved to be stable for only two weeks.

An NAD-containing adsorbent has been synthesised using the Dimroth rearrangement in one of the stages—transfer from the N(1) position in the purine ring to the exocyclic amino-group—for the AFC of dehydrogenases:[69]

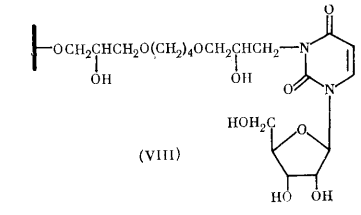


Thus the fairly ready alkylation of purines at the N(1) position in interaction with EAS-6B in weakly acid media (pH 5–6) can be regarded as an established fact; the subsequent Dimroth rearrangement leads to the immobilisation of the ligand at the exocyclic amino-group of the adenine ring.

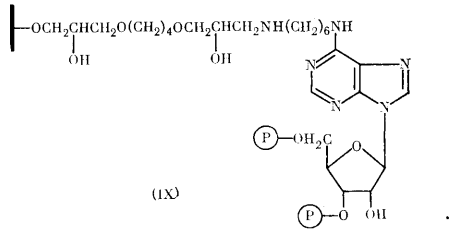
However, in a number of instances, particularly when the reaction is carried out in a strongly alkaline medium, the exact position in the polyfunctional ligand molecule at which the latter adds to EAS-6B is fairly difficult to determine. Thus, the adsorbent with adenosine immobilised on EAS-6B proved to be highly effective in the purification of deaminase.[61] The ligand was bound at pH 11.2 in 0.1 M sodium bicarbonate at 37 °C for 24 h and the authors believe that the ligand is most probably immobilised via the hydroxy-groups of ribose and not via the relatively unreactive amino-groups of adenine. Nevertheless, immobilisation via the exocyclic amino-group of the ligand is also apparently entirely feasible under these conditions—under similar conditions (Table 1) it has been possible to obtain the adsorbent with immobilised acriflavin (VII):[56]



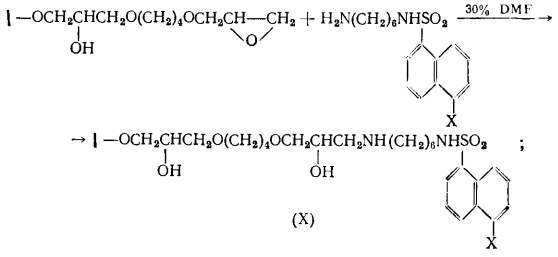
In similar cases, in the presence of several types of reactive groups in the ligand molecule, the proposed structures of the adsorbents probably cannot be regarded as finally established. Thus, Mitina et al.,[70,71] having established the covalent binding of uridine to EAS-6B at 37 °C in 0.1 M sodium hydroxide in the course of 16 h, describe only the postulated structure of the adsorbent (VIII) obtained:



More definite results were obtained after specific preliminary modification of the ligand molecule before immobilisation. For example, cAMP was initially converted into the C(8)-hydroxyethylthio-derivative, which was then readily coupled to EAS-6B at pH 11.[72] N(6)-ε-Amino-hexyl-3,5-ADP was analogously immobilised at pH 10 and 28 °C in the course of 20 h [73] and adsorbent (IX) was obtained:



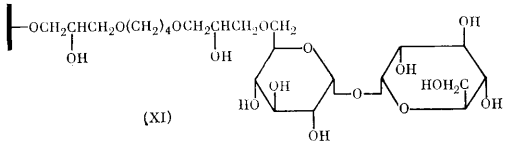
Derivatives of 1-sulphonaphthalene, which are calmodulin antagonists, have been immobilised at pH 9.8 in 30% dimethylformamide in the course of approximately 16 h at 40 °C via the amino-group of the hexamethylenediamine spacer, which had been previously introduced into the ligand molecule.[74] The adsorbent (X) synthesised contained approximately 20 μmoles of the ligand per ml of the gel.



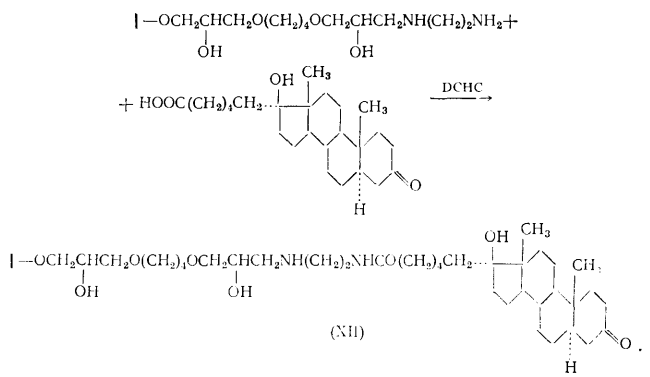
where X = H or Cl.

In connection with this synthesis, mention should be made of the organic solvent (dimethylformamide), which made it possible to obtain an adsorbent with a high capacity with respect to the ligand.

As stated above, carbohydrate ligands can be immobilised on EAS-6B without preliminary modification.[75,76] A detailed chemical study has been made[77] of the immobilisation of carbohydrates on EAS-6B. It was shown that the reaction proceeds mainly via the primary hydroxy-group and in the case of aminosugars it was found that the amino-group is six times more reactive in the reaction with the epoxy-group than the primary hydroxy-group. The preparation of a stable and effective adsorbent (XI) for the biospecific purification of proteins with a high affinity for non-reducing glucopyranosyl residues, by adding unprotected α,α'-trehalose to EAS-6B, has been described:[78]



The use of the short ethylenediamine spacer immobilised on EAS-6B for the subsequent coupling of the carrier to a carboxyl-containing steroid ligand by the carbodi-imide method has been described.[38] The adsorbent (XII) obtained was used for the isolation of steroid-binding serum proteins:



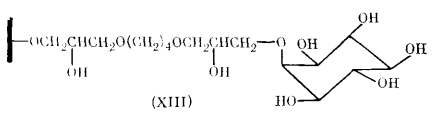
(XII)

An important feature of this synthesis was the use of CL-Sepharose, stable in non-aqueous media, because the ligand was immobilised in a 1 : 1 dioxan–dimethyl–formamide mixture with the aid of dicyclohexylcarbodi-imide (DCHC).

The use of EAS-6B for the synthesis of metal chelate adsorbents has been described.[79,80] The addition of the disodium salt of iminodiacetic acid has been achieved in 2 M sodium carbonate at 65 °C in the course of 24 h. The adsorbent obtained was used to purify nucleoside diphosphatase.[80]

S-Hexylglutathione–epoxy-Sepharose, in which the ligand was immobilised via its amino-group (pH 12, 30 °C), proved to be an interesting adsorbent based on EAS-6B. The unreactive epoxy-groups were blocked by 1 M ethanolamine in the course of 16 h. Several enzymes (glutathione-*S*-aryl transferase[81] and glyoxalase[57]) were purified on this adsorbent and in the latter case the yield of the enzyme was higher than on the adsorbent obtained by activating Sepharose with bromocyanogen.

According to Fazideen and Breitenbach,[82] it was possible to use EAS-6B in the immobilisation of the ligand in an organic solvent (dimethyl sulphoxide), although only in the course of a limited period (1 h at approximately 20 °C). The adsorbent (XIII) obtained was used for the purification of myoinositol oxygenase.

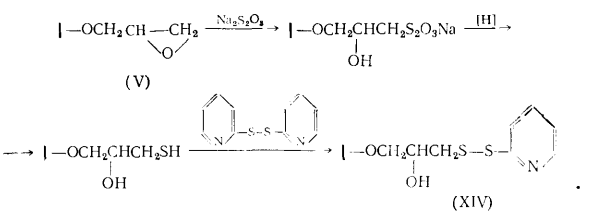


(XIII)

EAS-6B proved to be a convenient carrier for the immobilisation of *m*-aminophenylboronic acid.[83] The adsorbent synthesised bound effectively nucleotides, probably via the formation of a complex with the α-glycol group of ribose, and was investigated in this form by the authors with the aim of purifying several dehydrogenases.

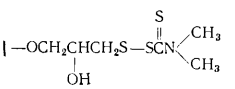
The covalent coupling to EAS-6B of other low-molecular-weight ligands, such as carbohydrate derivatives (*N*-acetyl-*D*-glactosamine,[60] *N*-acetyl-β-*D*-glucosamine,[41] tri-*N*-acetylchitotrioses,[41] cyclohepta-amyloses,[84] and β-*L*-fucosylamine[85]), an aminoalcohol (choline),[86] etc.

(b) *Adsorbents based on 1,2-EPS.* This type of epoxy-Sepharose[35] generally requires the introduction of an additional spacer in the immobilisation of the ligand. 1,2-EPS was first used to synthesise an adsorbent for covalent chromatography—"thiopropyl-Sepharose" (XIV),[35] which was obtained in accordance with the following scheme:



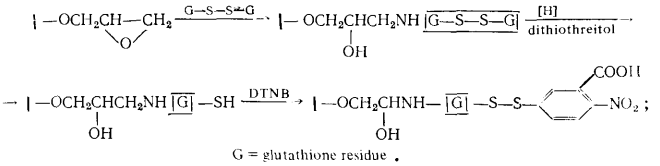
(XIV)

It is of interest to note that derivatives of di(2-pyridyl) disulphide with nitro- and carboxy-groups have also been investigated as ligands.[87] As expected, these derivatives of thiopropyl-Sepharose proved to be somewhat more active in thiol–disulphide exchange reactions and can be used in covalent chromatography together with the commerical adsorbent. The adsorbent (XV) with the dimethyldithiocarbamate residue as the ligand was obtained in the same study:



(XV)

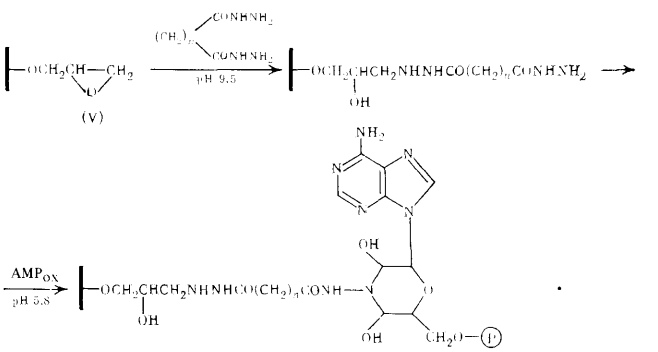
Epoxy-analogues of "activated thiol-Sepharose", the second commercially available adsorbent for covalent chromatography, have also been synthesised. Cystamine, cysteine, and glutathione residues were used as spacers and the ligand was the residue of 5,5′-dithiobis(2-nitrobenzoic) acid (DTNB).[43] The synthesis of the above adsorbents is indicated schematically below:



G = glutathione residue.

The use of adsorbents for the isolation and purification of SH-containing peptides and proteins has been examined in detail in a review.[18]

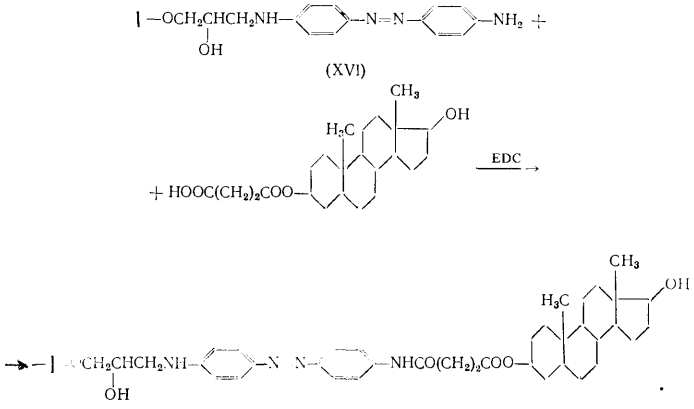
Using dicarboxylic acid hydrazides as spacers, a series of derivatives of hydrazidohydroxypropyl-Sepharose were obtained to which periodate-oxidised[88] nucleotides, for example, adenine and guanine nucleotides,[89] and NADP[43,90,91] were smoothly coupled. The dihydrazides are immobilised on 1,2-EPS at pH 9.5 at approximately 20 °C in the course of 10–16 h.[89] The subsequent addition of the oxidised nucleotides takes place via the ribose ring:



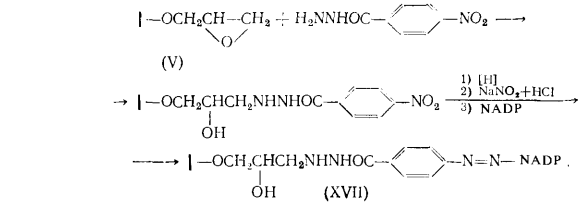
The hexamethylenediamine spacer was used for the immobilisation on 1,2-EPS of certain aminoacids[92] in the form of their *N*-hydroxysuccinimide esters. According to

Streikuviene et al.,[93] nonyloxypropyl-Sepharose proved to be most effective for the purification of phospholipase *D*.

The use of 4,4'-azodianiline as a spacer,[94] which was coupled to 1,2-EPS in 50% dimethylformamide in the course of 2 h, is of interest. The resulting coloured product (XVI) was coupled to the succinylated derivative of androstanediol in the presence of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC):

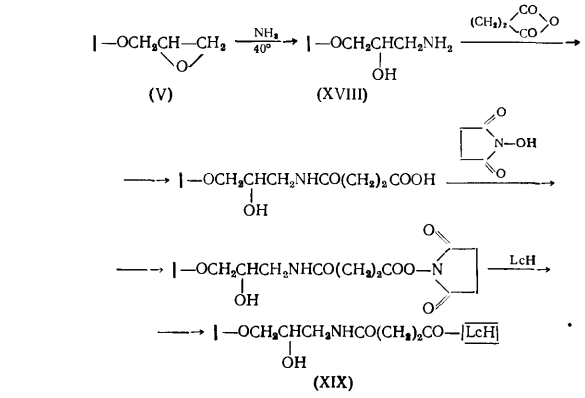


The syntheses of a series of adsorbents with an azo-linkage based on 1,2-EPS have been described. One of the examples of this kind is the preparation of NADP-azobenzo-hydrazidohydroxypropyl-Sepharose (XVII) in accordance with the following scheme:[95]



The spacer (*p*-nitrobenzohydrazide) immobilisation reaction on 1,2-EPS was carried out in aqueous dimethyl sulphoxide.

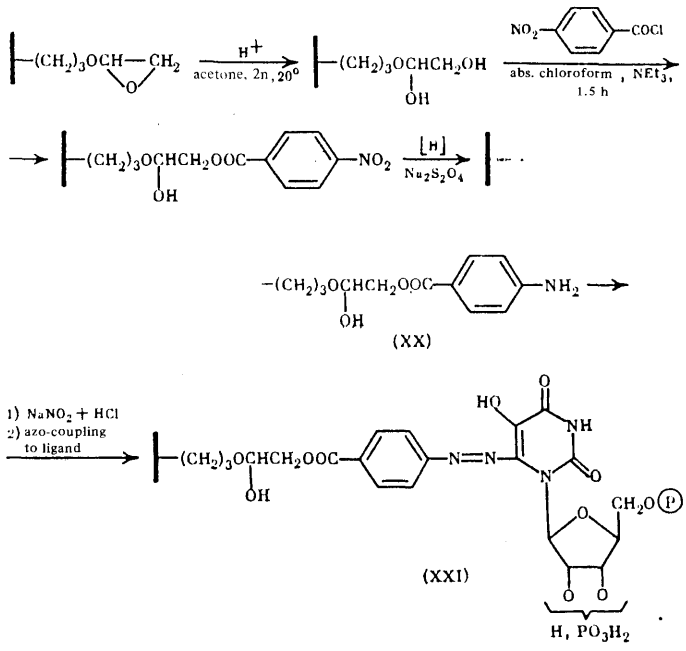
The amination of 1,2-EPS and EAS-6B has been achieved recently[96] in concentrated ammonia at 40 °C in the course of 2 h and amino-Sepharose (XVIII) and some of its derivatives were obtained for the first time. Thus, after the succinylation stage,[97] it was possible to obtain a highly stable affinity adsorbent (XIX) with hemagglutinin (LcH) as the ligand:



The amide and ester linkages in the adsorbent (XIX) proved stable at pH 9.8 (borate buffer solution). Nor are they ruptured when detergent solutions are used as eluents. Glucosamine-succinyloxypropyl-Sepharose has been obtained via an analogous scheme.[98]

The use of 3-amino-2-hydroxypropyl-Sepharose, obtained by the epoxidation of an agarose carrier with epichlorohydrin by means of a modified method[42] (25 °C, 4 h) followed by treatment with a 2 M ammonia solution for 16 h, for the immobilisation of a steroid ligand, namely 17β-hydroxy-3-oxo-5α-androstane-17α-(6-hexanoic acid) has been described.[99] The ligand was coupled to the amino-Sepharose in 70% aqueous dioxan in the presence of EDC.

(c) *Adsorbents based on silica carriers.* There have been no systematic studies of this group of EAC for the immobilisation of low-molecular-weight ligands. An investigation[34] of the immobilisation of 5-hydroxyuridine 2'(3'),5'-diphosphate on alusil in order to obtain an affinity adsorbent for the isolation of endonuclease A5 is of considerable interest. The azo-adsorbent based on epoxidised alusil was synthesised in accordance with the following scheme:



The content of amino-groups on the aminoaryl derivative (XX) was 133 μmol g^{-1} and the capacity of the azo-adsorbent (XXI) with respect to the nucleotide was 36.5 μmol g^{-1}. According to the authors' data, the adsorbent synthesised exhibited virtually no non-specific sorption and was extremely stable: after six isolation cycles, up to approximately 98.3% of the initial amount of ligand immobilised on the carrier remained. The possibility of employing in the syntheses of azo-adsorbents based on silicas of other spacers described [the *p*-nitrobenzohydrazide spacer[95] and spacers obtained on the basis of the hydrazides of *N*-(*p*-nitrobenzoyl)-ε-aminocaproic acid and *N*-(*p*-nitrobenzoyl)-glycylglycine] must be emphasised.[100]

2. Immobilisation of Polymeric Ligands

The immobilisation of polymers and biopolymers of different classes on EAC has not been studied in detail, although the necessity for such investigations is evident. The available literature data on this question are extremely scanty and scattered. EAS-6B has been usually employed for this purpose because of the presence in a carrier of this type of a long spacer, which ensures a fairly high reactivity of the carrier in reactions with biopolymers and the necessary steric accessibility of the immobilised ligand.

Lipopolysaccharides,[101,102] antibodies to human leukocytic interferon,[103] glycoproteins,[96] cellular material,[104] inhibitors of trypsin and trypsin-like enzymes,[27] polysaccharides,[76] and polynucleotides[105,106] have been covalently coupled to EAC as ligands. After the preliminary modification of its active centre with citraconic anhydride, ovomucoid was coupled to EAS-6B at pH 10 in the course of 16 h at 40 °C.[107] The percentage binding of the trypsin-like enzymes by this epoxy-adsorbent proved to be 92% compared with 30% for Sepharose activated with cyanogen bromide.

According to the data of Ustav et al.,[105] the periodate-oxidised t-RNA has been successfully immobilised on hydrazidoadipoyl-EAS-6B.

A simple and effective method of attaching DNA to epoxycellulose has been proposed.[39] The biopolymer was immobilised in 0.1 M sodium hydroxide at 20 °C in the course of 2 h. The DNA content in the resulting adsorbent was approximately 40 mg per ml of the gel. The adsorbent was distinguished by high stability with respect to organic solvents—ethanol, dimethylformamide, dioxan, toluene, etc., and also 2 M sodium chloride or 0.1 M sodium hydroxide in the course of 24 h at approximately 20 °C. The efficiency of the binding of polynucleotides varied in the sequence poly(dT) > poly(dC) = poly(dA) > poly(dG).

Studies of the conditions governing the immobilisation of peptides and proteins on EAC are of definite interest. Thus the optimum conditions for the attachment of glycyl-leucine to EAS-6B (pH 11, 50 °C in the course of 15 h) have been investigated.[27] The optimum binding conditions for the inhibitor of soya bean trypsin involve treatment in 0.5 M carbonate buffer solution at pH 9.5 and 25 °C for 24 h. The cell membrane proteins were immobilised on EAS-6B under similar conditions in the preparation of immunoadsorbents:[104] 0.05 M borate buffer solution at pH 9 in the course of 16 h at approximately 20 °C.

The data presented above suggest that biopolymers are immobilised on EAC under approximately the same conditions (alkaline medium, temperature 20–30 °C) as the coupling of low-molecular-weight ligands. The adsorbents obtained are as a rule highly stable.

A more detailed study of the processes involving the coupling of peptides and proteins to EAC, in particular GMG§, has been undertaken.[33,47] The author showed that a peptide of the type of glycyl-leucine is bound preferentially to GMG via the α-amino-group and the maximum degree of binding is observed after 72–96 h at 25–37 °C. The process proved to depend greatly on the pH with an optimum at pH 9.7. The capacity with respect to the ligand was approximately 20 μmol g^{-1}. The bond between the matrix and the ligand proved to be extremely strong: even acid hydrolysis under severe conditions led to the appearance of only trace amounts of glycine. On the other hand, the binding of the epoxy-groups of the carrier to the carboxy-groups of the ligand was independent of the pH. The ester linkage formed was hydrolysed in the usual way.

§Glycidyl methacrylate gel (Ed.of Translation).

In the immobilisation of serum albumin and trypsin on GMG, the maximum degree of binding of these proteins was found in an acid medium at pH 3, which suggested the important role of carboxy-groups in the coupling processes. The involvement of the lysine ε-amino-groups in the proteins investigated in the binding processes is manifested in the pH range 7–11. According to the authors, the immobilisation via the ε-amino-group is independent of the pH. The capacity with respect to the ligand of the adsorbents obtained at pH 8–11 was 3–4 times lower than for the adsorbents synthesised at acid pH. Apart from trypsin and albumin, it proved possible to immobilise also amino-glucosidase on GMG in an acid medium.[106] Subsequently it was shown that polymers with indole and phenol groups were effectively bound in an acid medium.[67] The optimum binding of indole-containing derivatives was observed at pH 3.85, the binding efficiency diminishing with increase of pH. Imidazole-containing derivatives had a binding optimum at pH 8.15.[33] For derivatives containing a primary amino-group, the binding optimum was detected at pH 9.55.

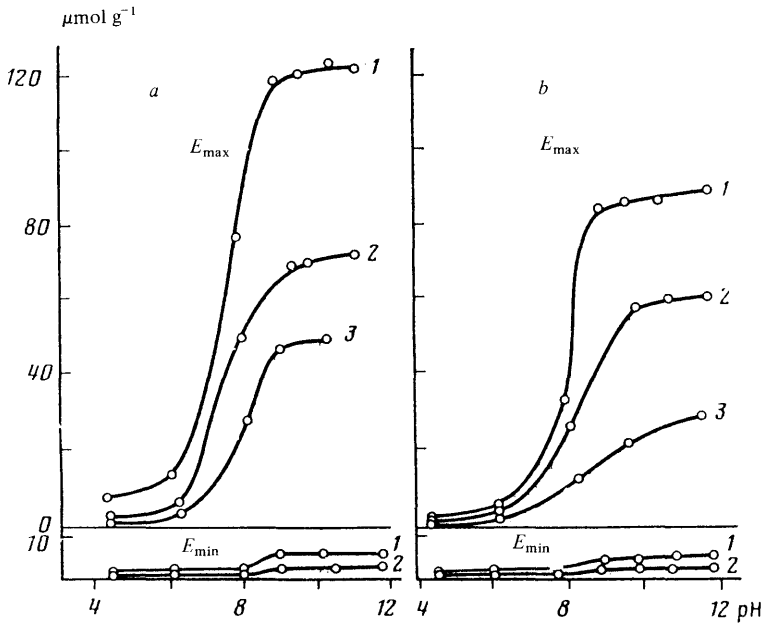
Data obtained in the study[33] of the influence of the nature of proteins on their immobilisation on EAC are of great interest. It was found that not only the binding conditions and the nature of the protein ligand but also the type of the polymer matrix are important in immobilisation. The results of these studies are presented in Table 2.

Table 2. Optimum pH for the immobilisation of certain proteins on various types of EAC.[33]

Immobilised protein*	Type of EAC**				
	porous glass	silica carrier	EAS-6B	GMG	Oxiranacrylic carrier
Serum albumin (4.9)	4 (45), 8.5 (20)	5 (50)	8 (300)	5 (20), 8 (10)	4—10 (50)
Papain (8.7)	8.5 (60)	8 (40)	9 (300)	7 (25)	—
Antilysin (10)	10 (80)	10 (20)	10 (300)	10 (15)	9.5 (100)
Trypsin (10.1)	8.5 (10)	3 (20)	11 (20)	3 (5)	10 (20)
Chymotrypsin	7—8 (50)	7—8 (20)	11 (40)	3 (10), 10 (5)	—

*The isoelectric point is indicated in brackets.
**The amount of immobilised protein in mg per gram of carrier is indicated in brackets.

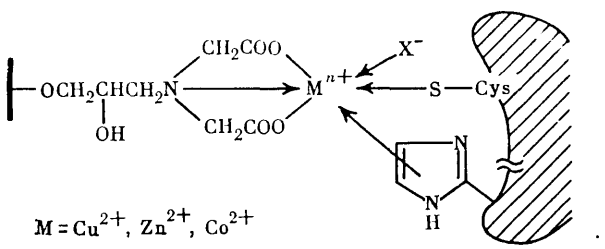
It follows from Table 2 that EAS-6B shows the maximum capacity with respect to the ligand and that only for this matrix was the immobilisation pH always in an alkaline region (pH 8–11). Such non-selectivity with respect to the nature of the immobilised protein should apparently be attributed to the effect of the spacer, which has the maximum length for the given type of EAC—12 carbon and oxygen atoms. Similar results have been obtained also for the oxiran-acrylic carrier. On the other hand, GMG and the adsorbent based on silica are the most sensitive to the nature of the immobilised protein and their capacity with respect to the ligand is low—for GMG it is lowest among all the EAC investigated. For certain proteins a clear-cut relation is observed between the isoelectric point and the optimum pH for immobilisation (for example, in the case of antilysin and to a lesser extent papain and albumin). According to the authors, the results for antilysin can be explained by the absence from this protein of tryptophan which tends to bind in an acid medium.



Dependence of the attachment of glycyl-D-phenylalanine to Separon H 300 (*a*) and Separon H 1000 (*b*), activated with epichlorohydrin, on the pH and reaction time; E_{max} = carriers activated to the maximum extent (1550 μmol g^{-1} for Separon H 300; 1700 μmol g^{-1} for Separon H 1000); E_{min} = carriers activated to the minimum extent (240 μmol g^{-1} for Separon H 300; 140 μmol g^{-1} for Separon H 1000); *1*) 48 h; *2*) 24 h; *3*) 12 h.

An analogous investigation has been carried out on epichlorohydrin-activated hydroxyalkyl methacrylate gels.[48] A study was made of the coupling of various amino-derivatives as a function of the pH, the reaction time, the ligand concentration, the degree of epoxidation of the carrier, and the chemical structure of the ligand. The Figure illustrates the dependence of the coupling of glycyl-D-phenylalanine on various types of epoxy-activated Separons on the pH of the medium and the reaction time.[48]

The covalent immobilisation of albumin and NAD-pyrophoshorylase on EAS-6B took place at 4 °C in the course of 28 h.[109] A number of enzymes (peroxidase, α-amylase, α-chymotrypsin, and glucose isomerase) have been recently immobilised using graft-polymerisation.[51] The method of non-covalent immobilisation for certain enzymes containing imidazole and thio-groups on an epoxy-activated metal chelate carrier is of definite interest.[44] The authors proposed the following structure of the carrier–enzyme complex:



Alkaline phosphatase and malate and lactate dehydrogenases have been immobilised in this way.

IV. THE APPLICATION OF ADSORBENTS BASED ON CARRIERS ACTIVATED BY EPOXY-COMPOUNDS IN AFFINITY CHROMATOGRAPHY

One of the main advantages of EAC is the simplicity of the preparation of affinity of adsorbents on their basis, the process involving only one stage in many instances. The biospecific adsorbents synthesised are exceptionally stable and are hardly hydrolysed in an alkaline medium. Thus the adsorbent with cAMP, immobilised on EAS-6B via the alcoholic hydroxyl, lost only approximately 0.04% of the ligand after storage in borate buffer solution for six months at 4 °C.[72] Immunoadsorbents based on EAS-6B lost the radioactive ligand to the extent of only 0.04–0.02%, while the percentage loss of radioactivity for the analogue based on Sepharose activated with bromocyanogen was 0.6–1.1% under the same conditions.[103] The complete absence of the scission of the coenzyme during the storage of NAD-containing epoxy-adsorbents compared with the bromocyano- and azo-derivatives has been demonstrated.[69]

A second important advantage of the adsorbents based on EAC is their high biospecificity owing to the hydrophilic nature of the spacer and the absence of additional ionogenic groups. As a consequence of this there is a possibility of employing adsorbents of this kind at earlier stages in the isolation and purification of biopolymers. For example, the direct use of thyroxine-epoxy-Sepharose[110] for the AFC of the serum in the early stages of the purification proved successful in the isolation of thyroxin-binding globulin. A 1000-fold purification of the test protein with a yield of about 70% was achieved. A fairly high degree of purification in the AFC stage (by a factor of 600) was retained also after the preliminary chromatography of the serum on hydroxyapatite.

Epoxy-activated Separon 1000 with the methyl ester of L-phenylalanyl-D-phenylalanine attached as the ligand has been used for the AFC of pepsin and proteinases from *Aspergillus oryzae*.[48] The high mechanical stability of the adsorbent made it possible to carry out the analytical AFC of pepsin under high pressure.

8-Aminoxanthine-epoxy-Sepharose showed a high selectivity in the single-stage isolation of the enzyme urate oxidase.[55] The degree of purification was by a factor of 88, the yield of the enzyme reached 93%, and the eluent was a 5 mM solution of uric acid.

The maximum degree of purification of cholinephosphate cytidylyltransferase on an EAS-6B-based adsorbent was by a factor of approximately 250 in the AFC stage with an overall yield of 59%.[62] A similar degree of purification (by a factor of 200) has been observed in the isolation of glutathione reductase on NADP-hydrazidoadipoylhydroxypropyl-Sepharose.[111] It is important to note that the adsorbent employed in the above study proved to be highly selective with respect to glutathione reductase (the arsenic-resistant fraction) and hardly bound the thiol-disulphide enzymes of the arsenic-sensitive fraction. An effective express method has been developed with the aid of this adsorbent for the preparation of almost homogeneous glutathione reductase.[111] It is remarkable that in both cases the AFC was carried out directly with the supernatant isolated after fractionation with ammonium sulphate. A simple and rapid three-stage method for the purification of α-amylase from triticale included in the last stage AFC on cyclohepta-amylose-epoxy-Sepharose.[84] It resulted in a final purification of the enzyme by a factor of 143 with an overall yield of about 33%.

In a number of studies the AFC on epoxy-sorbents was used in the concluding stages of the purification. Thus the application of pteridine-epoxy-Sepharose in the last (fifth) stage of the isolation of phenylalanine hydroxylase from rat liver permitted a degree of purification of the enzyme in the AFC stage by a factor of about 30.[66] The overall degree of purification was by a factor of 510 and the yield was 98%. The final phenylalanine hydroxylase preparation contained an admixture with catalase activity. AFC on *S*-hexylglutathione-epoxy-Sepharose was used in one of the stages of the purification of glyoxalase[57] and chromatography on this adsorbent led to an enzyme with a higher specific activity than purification on the adsorbent based on the bromocyanogen-activated Sepharose.

The use of metal chelate adsorbents based on epoxy-Sepharose has been described.[80,112-114] The purification of nucleoside diphosphatase by a factor of 194 and with a yield of about 16% has been achieved on these adsorbents.[80] The eluent was a 15 mM solution of L-histidine in 10 mM maleate buffer solution.

It is known that adsorbents based on EAC are widely used also in hydrophobic chromatography. Studies of the relation between the chemical structure of the adsorbents and the characteristics of the adsorption of various proteins are of definite interest. Studies[45,46] of blood proteins established the following general features. Adsorbents with lengths of the alkyl chain ranging from C_1 to C_5 gave rise to a relatively low degree of adsorption of blood proteins, while an increase in the hydrophilicity and polarity of the ligand by the introduction of hydroxy-, methoxy-, or cyano-groups greatly reduced the degree of adsorption. The maximum decrease was observed after the introduction of the cyano-group. On the other hand, the presence of a positive charge in the ligand molecule (a quaternary ammonium group) increased the degrees of adsorption of all the proteins investigated. It must be emphasised that the optimum lengths of the hydrocarbon chain in the ligand are different for different proteins. Fibrinogen, thrombin, and globulin have a binding optimum on the ligand with a C_7 chain, while for albumin and immunoglobulin G the adsorption optimum is on the ligand with a C_8 chain. The presence of branches in the ligand decreases the degree of adsorption.

The isolation of prephenate dehydratase has been achieved using adsorbents with a hexamethylenediamine spacer and certain aminoacids as ligands.[92] *N*-Acetylated derivatives of these adsorbents lost their capacity to bind the enzyme. At the same time the enzyme could be desorbed only from the aminohexyl and glycylaminohexyl analogues of 1,2-EPS (in 0.5 M sodium chloride or 140 mM hexamethylenediamine).

A study[115] undertaken to screen the affinity adsorbents for the isolation of inorganic pyrophosphatase[115] showed that hexylepoxy-Sepharose with a high ligand concentration (40 μmol ml^{-1}) strongly bound the enzyme with a complete retention of its pyrophosphatase activity. The protein could not be eluted (1 M sodium chloride, substrate). On the other hand, the bromocyanogen analogues of the adsorbent (admittedly with a ligand concentration lower by a factor of 4–7) bound the enzyme much less strongly. It was readily eluted from these adsorbents with 0.05–0.1 M sodium chloride solution.

A number of studies have been published recently concerning the use of commerical Octyl-Sepharose and phenyl-Sepharose for the hydrophobic chromatography of many biopolymers, for example, choline acetyltransferase,[116] specific endonucleases,[117] alkaline phosphatase, and 5'-AMP nucleosidase,[118] and restriction endonuclease REcoCK,[119] and also for the separation of the phospholipid and protein components of complex III of the respiratory chain of mitochondria,[120] for the immobilisation of trypsin with preliminary modification of the enzyme,[121] for the isolation of microsomal cytochrome P-450,[122] for the investigation of cobalamin-binding proteins,[123] for the purification of calmodulin,[124] etc.

It has been noted that in certain cases where adsorbents based on Sepharose activated with cyanogen bromide are used the ligand undergoes appreciable bioinactivation, while the analogous epoxy-adsorbent retains a satisfactory affinity for the biopolymer isolated.[107] Thus in the AFC of a trypsin-like enzyme the highest percentage binding was achieved for the adsorbent based on EAS-6B (92%).

Thiopropyl-Sepharose is one of the adsorbents widely used in covalent chromatography.[35] The spectrum of its applications is fairly wide, encompassing the isolation of thiol-containing proteins,[125,126] thiol-containing peptides,[127] and mercurated polynucleotides.[128] The possibility of separating two similar thiol-disulphide oxidoreductases, protein disulphide isomerase, and glutathione-insulin transhydrogenase by covalent chromatography on thiopropyl-Sepharose has been demonstrated.[129] The supernatant was subjected to preliminary purification by fractionation with ammonium sulphate, gel-filtration on Sephadex G-200, and ion-exchange chromatography. The eluents for covalent chromatography were thiols with an increasing reducing capacity—20 mM L-cysteine, 50 mM reduced glutathione, and 20 mM dithiothreitol. The employment of thiopropyl-Sepharose made it possible[130] to separate highly reactive thiols, for example, cysteine proteinase from *Actinidia chinensis*, from the remaining thiol-containing components. The application of reduced thiopropyl-Sepharose in the purification of cytoplasmic aldehyde dehydrogenase involving the removal of an admixture of mitochondrial proteins has been described.[131] The same adsorbent modified with 2-hydroxy-5-nitrobenzyl bromide was used for the immobilisation of α-chymotrypsin

and β-amylase.[132] The problems of the application of covalent adsorbents are specifically considered in a review.[18]

The principal studies dealing with the applications of adsorbents based on EAC in AFC are listed in Table 3.

Table 3. The application of adsorbents based on EAC for the isolation and purification of biopolymers.

Ligand (spacer)	Biopolymer isolated source)	Refs.
	EAS-6B	
Inhibitor of osya bean trypsin	Trypsin (commercial preparation)	[27]
Ovomucoid	Trypsin-like enzyme (from *Streptomyces erethreus*)	[107]
Myoinositol	Myoinositol oxygenase (from rat kidneys) myoinositol kinase (from *Lemna gibba*)	[82]
Adenosine 3′,5′-diphosphate (hexamethylenediamine)	Succinate thiokinase (from pig heart)	[73]
Choline	Choline and enthanolamine kinases (from rat liver)	[86]
8-Hydroxyethyl-cAMP	Regulatory subunit of protein kinase	[72]
S-Hexylglutathione	Glutathione S-transferase (from human placenta)	[81]
Reduced glutathione	Glutathione S-transferase (from human liver)	[63]
Glycerylphosphoryl choline	Cholinephosphate cytidylyltransferase (from rat liver)	[62]
Ribose-5-phosphate, neopyrithiamine, thiamine pyrophosphate, hydroxythiamine	Transketolase (from *Candida utilis* and baker's yeast)	[59]
Adenosine	Adenosine deaminase (from human erythrocytes)	[61]
S-Hexylglutathione	Glyoxalase I (from rabbit liver)	[57]
2-Amino-4-hydroxy-6,7-dimethyl-5,6,7,8-tetrahydropteridine	Phenylalanine hydroxylase (from rat liver)	[66]
Trimethoprim and its analogues	Dihydrofolate reductase (from *E.coli*)	[53]
Aminomethyl-4-anilino-5-methoxy-1,2-benzoquinone	Menadione reductase (from rat liver)	[65]
8-Aminoxanthene	Urate oxidases (from ox liver, rat liver, and yeast)	[55]
Folic acid	Ribonuclease A (from ox pancreas)	[54]
Ditto	Endonucleases EcoRI (from *E.coli*) and BglII (from *Bacillus globiggii*)	[117]
NAD^+ or NADH	Alcohol and lactate dehydrogenases	[69]
3-Aminophenylboronic acid + nucleotides and coenzymes	Dehydrogenases	[83]
Cyclohepta-amylose	α-Amylase (from a hybrid of wheat and full flax)	[84]
Aminomethyl-, 4-aminobenzyl-, and *N*-(4-aminobenzyl)-4-aminobenzyl-phosphonic acids	Alkaline phosphatase (from ox small intestine)	[64]
Arabinan	α-L-arabinofuranosidase (from *Aspergillus niger*)	[76]
Iminodiacetic acid + Cu^{2+}	Nucleoside diphosphatase (from rat liver)	[80]
Ditto	Lactoferrin (from human milk)	[112]
Iminodiacetic acid + Zn^{2+}	Alpha$_2$-SH-glycoprotein (from human plasma)	[113]
D-Galactosamine	β-Galactosyl-binding lectin (tridacnin) from *Tridacna maxima*)	[58]
Trehalose	Concanavalin A (from *Canavalia ensiformis*)	[78]
N-Acetyl-D-galactosamine, *N*-acetyl-D-glucosamine	Lectins (from soya beans and wheat seedlings)	[60]
Tri-N-acetylchitotriose, methyl *N*-acetyl-β-D-glucosaminide	Agglutinin (from *Solanum tuberosum*)	[41]
17β-Hydroxy-3-oxo-5α-androstane-17β-(6-hexanoic acid) (diaminoethyl)	Steroid-binding protein (from human serum)	[38]
Auxin analogues	Auxin-receptor proteins	[68]
Thyroxin	Thyroxin-binding protein (from human serum)	[110]
N-(6-Aminohexyl)-5-chloronaphthalene-1-sulphonamide	Calmodulin and calcium-binding protein S-100 (from ox brain)	[74]
Agglutinin from *Ricinus communis*	Tyroglobulin	[41]
t-RNA (hydrazidoadipoyl)	Ribosomal proteins	[105]
Iminodiacetic acid + Zn^{2+}	Interferon (from human fibroblasts)	[114]
Interferon from human leukocytes	Corresponding antibodies	[103]
β-Ecdysone	Proteins of the corresponding antiserum	[133]
Lipopolysaccharides from *Shigella sonnei*	Homologous antiserum, bacteriophage SKVI	[101]
Membrane material from human lymphoblastoid cells	Corresponding antibodies	[104]
	EAS-6B and 1,2-EPS	
Haemagglutinin (succinyl)	Glycoproteins	[96]
	1,2-EPS	
2-Thio-4-(nitro, carboxy)pyridine; tetramethylthiuram disulphide residue	Cysteine peptides, mercaptalbumin, papain, urease, ox serum albumin, pancreatic ribonucleases	[87, 127]

Table 3 (cont'd.).

Ligand (spacer)	Biopolymer isolated (source)	Refs.
2-Nitro-5-thiobenzoic acid (aminoethyl, glutathione, cysteine)	Glutathione reductase (from rat liver)	[43]
NADP (*p*-azobenzohydrazide)	Ditto	[95]
Ditto or NADPH (hydrazidosuccinyl, hydrazido-adipoyl)	"	[90, 91, 111]
Aminoacids (hexamethylenediamine, succinyl)	Prefenate dehydratase	[92]
3-Hemisuccinate of 5α-androstane-3β, 17β-diol(4,4′-azodianiline)	Testosterone-oestradiol-binding globulin (from human plasma	[94]
Cortisol, 5α-dihydrotestosterone	Steroid-binding proteins	[134]
Adenine and guanine nucleotides (hydrazidoadipoly)	Elongation factor Tu (from *E.coli* MRE 600)	[89]
Alkyls, hydroxy(alkoxy)alkyls, and their cyano- and carboxy-derivatives	Albumin, globulin, fibrinogen, prothrombin	[45, 46]
Thiopropyl	Protein disulphide-isomerase (from ox liver), glutathione-insulin transhydrogenase (from ox liver)	[126, 129]
Ditto	Actinidin (from *Actinidia chinensis*)	[130]
"	Copper-binding proteins from human liver	[125]
	Amino-1,2-EPS	
Lactose, melibiose, maltose, *N*-acetylchitotetraose; glucosamine, galactosamine(succinyl)	Agglutinins (from soya, *Arachis hypogaea*, wheat seedlings, etc.)	[98]
17β-Hydroxy-3-oxo-5α-androstane-17α-(6-hexanoic acid)	Androgen-binding protein (from rat epididymis)	[99]
	Epoxycellulose	
Deoxyribonucleic acid	Polynucleotides, complementary m-RNA (from bird liver)	[39]
	GMG	
Trypsin	Trypsin inhibitors	[47]
	Epoxy-separon H 1000	
Methyl ester of L-phenylalanyl-D-phenylalanine (ε-aminocaproyl)	Pepsin and proteinases (from *Aspergillus oryzae*)	[48]
	Silica(alusil)	
5-Hydroxyuridine 2′(3′), 5′-diphosphate (*p*-azobenzoyl)	Endonuclease A5 (from actinomycetes)	[34]

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The data described above show that biospecific adsorbents based on EAC constitute one of the commonest types of adsorbents currently used in AFC and related methods. One sometimes encounters the view that AFC in a pure form does not exist at all and that the biospecific interaction of the biopolymer to be isolated with the sorbent in AFC is inevitably accompanied by a complicated set of interactions including non-specific electrostatic, hydrophobic, and other effects. Both AFC and associated methods, such as hydrophobic, covalent, and metal chelate chromatography are therefore incorporated in a single group of methods. This tendency carries the risk, both formal and purely theoretical, of an erroneous interpretation of the chromatographic results, particularly when the AFC method is used for the investigation of the mechanisms of biochemical reactions, for the determination of the constants for the association of biopolymers with low-molecular-weight ligands, etc. An arbitrary mixing of the methods, indicated above, for the isolation and purification of biopolymers can be caused, and this is not the least important cause, by the application in AFC, particularly for preparative purposes, of carriers such as porous glass, silochromes, and a number of others, which by their very nature can introduce into the purification process non-specific interactions which do not, however, prevent in many cases the attainment of a fairly high degree of purification of the biopolymer.

The efforts of investigators concerned with the further development of the AFC method will undoubtedly be directed to the elimination or reduction to a minimum of non-specific

effects in the chromatographic process, because this will make it possible to demonstrate fully the unique possibilities of the AFC method. For a clear-cut formal separation of the AFC method from other purification procedures, the term "bioaffinity chromatography" has been proposed.[10,135,136] The new methods for the activation of polysaccharide matrices which have appeared recently have been chosen to obviate the disadvantages of the method of bromocyanogen activation, which is still most widely used. These include the modification (based on the study of the reaction mechanism) of the bromocyanogen method itself,[137,138] the employment of reactive sulphonyl chlorides[139,140] and carbonylating reagents,[141,142] *O*-succinylation,[143] the application of activated chloroformates,[144] and a number of others. Activation by epoxy-compounds occupies an honourable place among these methods. Its evident advantages, namely simplicity, chemical strength of the bond formed, hydrophilicity of the adsorbents obtained, and elimination or reduction to a minimum of the charged groups of the adsorbent, promote the maximum approach of the interaction between the biopolymer to be isolated and the immobilised ligand to processes occurring under physiological conditions, i.e. the achievement of the idea of the AFC method in a pure form. One may also expect further extensive application of adsorbents based on EAC for the effective purification of biopolymers and as a refined instrument for biochemical research.

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Institute of Biological and Medical Chemistry,
Academy of Medical Sciences of the USSR,
Moscow

Kemerovo State Medical Institute

Russian Chemical Reviews

November 1984

Translated from *Uspekhi Khimii*, 53, 1769-1789 (1984)

U.D.C. 539.18+541.124.26

Structural Disorder and Mechanochemical Reactions in Solids

P.Yu. Butyagin

The present review is devoted to an analysis of the relationship between the changes in the structure and reactivity of solids, brought about by the development of a deformation. It has been shown that the principal regular features of mechanochemical transformations are determined by the extent of the structural disorder, the processes involved in its relaxation with the liberation of stored energy, and the mobility of the atoms. The part played by each of these factors has been examined for mechanically activated chemisorption, the ionisation of structural defects, the production of various non-equilibrium states on relaxation, the excitation of the mobility of the structure with the intensification of diffusion-controlled reactions, etc. The bibliography contains 87 references.

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I. INTRODUCTION

Deformation is the first response of a solid to the action of external mechanical forces. The external changes in the shape and dimensions of the solid reflect the changes in the order of the arrangement of the atoms, that is the structure of the substance with the development of the deformation. The nature of the internal changes depends on the type of solid and on the conditions of mechanical loading. They may be restricted to an increase or decrease in the interatomic distances, new defects (point, line, plane) may be produced, the type of crystal lattice may change, and in the limit the crystal may be transformed to an amorphous mass or, on the contrary, an amorphous substance may crystallise on deformation. Structural changes inevitably influence the structure-sensitive properties of a substance—its reactivity and transport phenomena (diffusion, thermal conductivity, electrical conductivity, etc.).

From the mechanochemical viewpoint, three aspects of these changes are important.

1. The structural disorder in the substance. The appearance of vacancies, interstitial atoms, and dislocations, which act as centres for the development of topochemical transformations, the production of broken bonds, which initiate various reactions, including chain processes, and the creation of chemically active freshly formed surfaces represent the most familiar examples illustrating the role of structural defects in the mechanical activation of solid reagents.

2. The second factor is structural relaxation, involving the most varied processes, which often have unexpected consequences. The wide variety of relaxation phenomena was revealed after the processes of deformation and breakdown in solids began to be studied by modern electrophysical and optical methods. The emission of fast electrons (with energy up to several keV, the Deryagin effect) and slow

electrons, mechanoluminescence, radiation in the radio and X-ray ranges, acoustic emission, the decomposition of a substance with the ejection of atoms and molecular fragments, and other phenomena have been discovered. It cannot yet be stated that all these phenomena are direct consequences of relaxation processes, but for each of them there exists at least one hypothesis relating the observed effect to the production, movement, and disappearance of structural defects. It should be noted that the energy liberated when defects disappear may reach several eV, that is it is quite sufficient for electronic excitation, ionisation, or bond rupture.

3. No less important is the third factor, which can be called the mobility or dynamics of the structure. In the development of a deformation, the new structure not only is formed, but also "lives". The internal stresses are weakened, and the forces of interatomic, intermolecular, or interionic interaction in the crystal are modified. Point defects are produced and displaced, dislocations multiply and move, grain boundaries are displaced, cracks appear and grow, etc. The mobility of the structure in the development of a deformation creates extremely favourable conditions for solid-phase chemical reactions.

Under real conditions, all three factors involved in the effect of deformation on the reactivity of a substance operate simultaneously. When the deformation of a substance and a chemical reaction are separated by an appreciable time interval, sufficient for the completion of relaxation processes, only the first factor—the existence of a changed structure in the substance—operates. The increase in reactivity due to stable changes in the structure of a substance is usually called mechanical activation.

There are also processes in which the principal rôle is played by the last factor, that is the mobility of the structure; these are associated with the intensification of chemical transformations in substances, where a reaction is possible, but the thermal motion, including translational diffusion, is completely "frozen", and the mobility of the particles, required for the reaction to take place, is brought about only by plastic deformation. The basic literature can be found in monographs, collected papers, and reviews.[1–20] The part played by structural disorder, its relaxation, and mobility in mechanochemistry is examined below for specific examples.

To compare the efficiencies of the action of the above factors, it is necessary to know the energy yield of the corresponding processes, since it is only in energy units that it is possible to compare the emission of electrons, the production of dislocations, luminescence, and chemical transformations. The measurement and calculation of these energy yields, which represent the quantitative basis of mechanochemistry, have not yet been sufficiently recognised; an exception is provided by ultrasonic chemistry.[21]

II. STRUCTURAL DISORDER

The treatment of various materials in mechanochemical reactors (apparatus for fine subdivision, the application of shock waves or pressure, shear combined with deformation, etc.) is accompanied by the production of structural disorder, which is preserved partly or completely for a fairly long time interval after the mechanical treatment has stopped. A clear and distinct indication of the extent of structural breakdown is provided by the change in the density of a substance after mechanical treatment. In quartz, the density decreases from 2.4 g cm^{-3} to 2.2 g cm^{-3},[13,22] corresponding to an increase in free volume by 8–9%. (For comparison it may be noted that the natural free volume of polymeric glasses is close to 2.5%.) These data reflect the state of quartz some time after mechanical treatment, when the structure has partly relaxed. During the development of the deformation, the extent of the decrease in the density of the substance is even greater, and the layer next to the surface is permeable to gases. The mechanically activated solubility of argon in quartz at 80 K and a pressure of 20 hPa is 10^{-2} mole kg^{-1}.[23] Similar effects are characteristic of metals, whose crystal lattices are much denser.[24]

In two-dimensional and one-dimensional systems such as highly anisotropic layer crystals and linear polymers, the degree of deformational disorder is even greater, and the state of limiting decrease in density may be frozen and preserved for study.[23,25] Since the excess free volume is so large that it is accessible to a gas, the extent of the disorder can be characterised by the sorptive capacity or the specific surface S, calculated using the BET equation from the isotherms for the reversible adsorption of argon or other gases at 80 K. The internal surface area generally corresponds to tens of hundreds of m^2 g^{-1}. In molybdenum disulphide (see Fig. 1*a*), thermal mobility of the atoms sufficient for healing appears at 150–200 K.

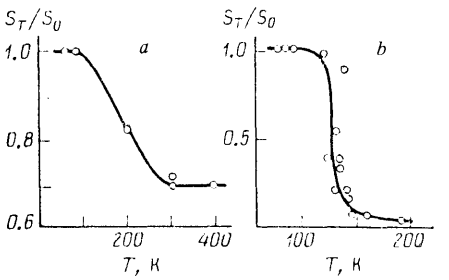


Figure 1. Thermal sintering of mechanically disordered powders of molybdenum disulphide (*a*) and polymethyl methacrylate (*b*);[23,25] S_0 and S_T are the specific surfaces at temperatures of 80 K and T.

The effect of structural disorder in polymers is even greater. For example, in polymethyl methacrylate after mechanical treatment at 80 K, the sorption of argon at a pressure of only 10 hPa is close to 10 mole kg^{-1}; the gas can be removed by evacuation, and adsorbed again. The internal surface area, calculated formally from the sorption isotherms, reaches 600–800 m^2 g^{-1}. The structure loosened to the maximum extent by deformation can be preserved for an unlimited time only at a temperature below 120 K (Fig. 1*b*). Above this temperature, spontaneous sintering begins, with a decrease in the internal surface area accessible to a gas by a factor of several hundred.[25] This extensive decrease in density is the clearest example of the effect of deformation on the structure of a solid.

The relationship between the changes in the structure and reactivity of a solid is important for mechanochemistry. Comparatively detailed information on the nature of mechanical defects, their concentration and reactivity, the direction of elementary reactions involving them, and the kinetic and thermochemical parameters has been obtained for the surface

of solids, where these defects are accessible to molecules from the gas phase. The friction and fracture surfaces of quartz,[15,26,27] silicon,[28] graphite,[29] and other crystals[30,32] have been studied.

Mechanically stimulated chemisorption on the surface of quartz has been described most systematically. The external manifestation of the phenomenon is that the initially inert surface of the solid, as a result of mechanical treatment, becomes chemically active in reactions with gases. Thus SiO_2, which is the highest oxide of silicon, does not react with oxygen under ordinary conditions; the product of the mechanochemical reaction is a previously unknown surface peroxide, assumed to have the structure $\equiv Si-O-O-O-Si\equiv$.[26] The formation of this peroxide can be represented as follows:

$$\equiv Si\cdot \quad \equiv SiOO\cdot \quad Si{=}O$$
$$+\ O_2 \rightarrow \quad +$$
$$\equiv SiO\cdot \quad \equiv SiO\cdot \quad Si{=}O$$

Oxygen is attached to the free radical $\equiv Si^{\bullet}$, produced at the point of mechanical rupture of the siloxane bond, after which the peroxide radical $\equiv SiOO^{\bullet}$ recombines with the $\equiv SiO^{\bullet}$ radical. The final result is that an oxygen molecule is "built into" the broken bond.

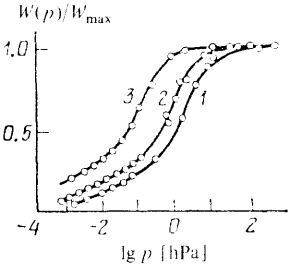


Figure 2. The mechanically activated chemisorption of hydrogen on the surface of quartz at different temperatures, K: *1*) 370; *2*) 300; *3*) 80.[26]

The regular features of mechanical chemisorption are illustrated by the graphs in Fig. 2. For a specific surface of quartz greater than 2–5 $m^2\ g^{-1}$, the reaction is initiated by friction, that is by deformations in the layer next to the surface of the powder particles.[26] The graph giving the dependence of the reaction yield on the gas pressure $W(P)$ has a characteristic inflection.[33] At a high pressure, when the frequency of the collisions of the gas molecules with the surface is high, the reaction yield $W(P)$ has its highest value and is independent of pressure. Under these conditions, all the structural defects produced are involved in the reaction, and the consumption of the gas characterises the number of active centres formed by the friction of the particles of the powder against one another. The energy yield of the formation of the short-lived active centres is 10^{-1}–10^{-2} mole MJ^{-1}. At a low pressure, when the collisions of the molecules with the surface are infrequent, some of the short-lived centres are able to disappear before reacting with the gas, so that the yield of the reaction decreases.

In the absence of a gas, that is on mechanical treatment of the powder in a vacuum, up to 6×10^{16} m^{-2} free radicals $\equiv Si^{\bullet}$ and $\equiv SiO^{\bullet}$ are stabilised on the quartz surface.[15,34] The structure and chemical properties of the free radicals on a quartz surface have been studied in detail by EPR, chemisorption and thermal desorption, microcalorimetry, and luminescence. Detailed information on the reactivity of mechanical radicals, including a description of the stepwise mechanism, the kinetic law, the rate constants, and the heats of the reactions with CO, O_2, H_2, CO_2, and various organic molecules, have been published.[15]

The free radicals $\equiv Si^{\bullet}$ and $\equiv SiO^{\bullet}$ are not the only defects produced mechanically on the disordered surface of quartz. A smaller number of silicon atoms with two broken bonds, that is silylene centres =Si:, are stabilised.[15] It has been suggested that =C: atoms exist on the fracture surface of graphite,[29] =Ge: atoms on the surface of germanium oxide,[30] and Sn^{2+} ions on the surface of tin oxide.[16,31,32]

An important contribution to chemical activity is made by deformed bonds, which act as carriers of residual internal stresses. They were first detected in the elongation of polymers.[18] Deformed siloxane bonds are observed from the displacement of the stretching band in the infrared spectra.[35] The chemical properties of the deformed bonds on a quartz surface are similar to those of the radical pairs $\equiv Si...OSi\equiv$. Thus hydrogen reacts with them practically instantaneously at 80 K; the activation energy of the reaction

$$\equiv SiO... Si\equiv + H_2 \rightarrow \equiv SiOH + HSi\equiv$$

does not exceed 2–3 kcal $mole^{-1}$;[26] such a low activation energy is characteristic of free-radical, and not molecular reactions. The deformed bonds readily undergo not only hydrogenation but also hydrolysis[36,37] and carbonation. The energy of deformation is liberated in all these reactions.

To determine the surface concentration of deformed bonds, they are titrated with H_2 and CO_2. For the same exposure in the gas, the quantity of bonds reacting with CO_2 is several times greater than the quantity reacting with H_2; the difference is due to the non-uniformity of the distribution of the stresses in the bonds and the corresponding distribution with respect to reactivities. Judging from the consumption of hydrogen,[26] the concentration of deformed bonds on the surface of mechanically activated quartz at 80 K is approximately ten times the concentration of radicals, and reaches $(4–6) \times 10^{17}$ m^{-2}.

The curves in Figs. 3*a* and 3*b* illustrate the thermal stability of the active centres on the surfaces of quartz and magnesium oxide.[15,26,38] The concentration of radicals is independent of temperature; their stability is determined primarily by the purity of the reaction system; the more thoroughly traces of moisture are removed, the more stable the radicals. As expected, the concentration of deformed bonds, reflecting the magnitude of the residual stresses, decreases with increase in temperature.

Thus the nature of mechanical chemisorption on the surface of covalent crystals can be represented as follows. The friction and fracture of the particles of the substance leads to the production of disorder in the surface and to the deformation and rupture of chemical bonds. At room temperature, the deformed bonds undergo a spontaneous decrease in length, and some of the radicals disappear under the influence of friction; thus the complete utilisation of the work done in producing the disorder requires the creation of conditions in which the rate of the reaction of gases with the surface is greater than the rate of disappearance of the short-lived active centres.[39]

The disordered surface of magnesium oxide, which is a stable ionic crystal with melting point ~2900 K, has a high concentration of chemically active centres [up to 1×10^{14} cm^{-2} in the reaction with H_2, and $(3–5) \times 10^{14}$ cm^{-2} in the reaction with CO [38]]; the active centres are stable in a vacuum at

room temperature (see Fig. 3*b*). Hydrogen on this surface dissociates to give atoms with the formation of Mg–H and Mg–OH groups.

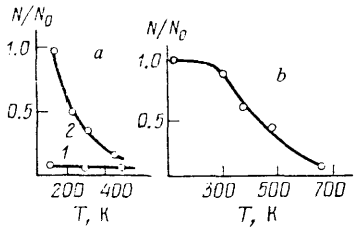


Figure 3. The thermal stability of the active centres on the surface of the oxides of silicon (*a*) (*1*—free radicals, *2*—deformed siloxane bonds) and of magnesium (*b*); N_0 and N_T are the initial and current concentrations of centres.[26,38]

For crystals made up of close-packed ions, the concepts of deformed and broken bonds become indefinite. Taking the extreme limiting case of a purely ionic structure (see Ref. 40, and also a criticism of this approach for alkaline earth metal oxides[41]), the high chemical activity of the disordered surface of MgO can be explained qualitatively as follows.[38] The MgO crystal consists of the chemically inert ions Mg^{2+} and O^{2-} with noble-gas electronic structures; these ions are energetically unfavourable in the free state. To obtain Mg^{2+} and O^{2-} ions in the gas phase from metallic magnesium and molecular oxygen, an energy of ~35 eV is required. When the small doubly-charged ions are close packed, however, there is a gain of electrostatic interaction energy, which more than compensates the loss. Thus the anions and cations are stable in the regular lattice, and the MgO crystal is inert and stable. After the mechanical production of disorder in the crystal, the packing of the ions becomes loose. The average number of neighbours of each ion becomes smaller, and the interatomic distances greater, compared with the regular lattice. Thus in the disordered regions there is a decrease in the strength of the electrostatic interaction responsible for the stability of the ions. Total loss of stability leads to the loss of an electron, that is to the conversion of the O^{2-} ion into the chemically active radical-ion O^-.

The stability of ions can be characterised by the energy required to transfer an electron from the anion to the cation:

$$Mg^{2+}O^{2-} \longrightarrow Mg^{+}O^{-} .$$

In a regular crystal, this energy, which is equal to the width of the band gap, is close to 8 eV. On a surface disordered by friction, the energy of electronic excitation should be smaller. In principle, it can be estimated from the position of the long-wave edge of the absorption band in the spectrum of the surface.

Fig. 4 gives the diffuse reflectance spectrum for a disordered MgO surface (curve *1*). The edge of the band corresponds to an energy of ~4–5 eV, compared with 8 eV for the regular crystal.[38] A similar effect was recently detected in other disordered oxides.[32] The displacement of the boundary of the absorption band by 3–4 eV can be regarded as a measure of the energy of disorder of the surface. After the chemisorption of hydrogen, as a result of which the most active parts of the surface are "worked out", the boundary of the spectrum is displaced to the left by ~1 eV (curve *2* in Fig. 4).

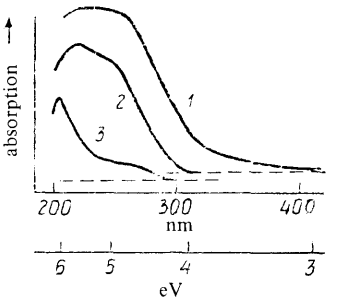


Figure 4. Diffuse reflectance spectra of magnesium oxide powders: *1*) after mechanical treatment; *2*) after reaction with hydrogen; *3*) after heating in a vacuum.[38]

The initial energy yield of the mechanically stimulated chemisorption of hydrogen for MgO is greater than that for quartz, and is equal to ~0.2 mole MJ^{-1}.[38] The excess energy of the disordered surface, calculated from the displacement of the long-wave boundary of the spectrum (by 3–4 eV) and the concentration of active centres (~5 × 10^{18} m^{-2}), is on the average 2–3 J m^{-2} or 100 kJ $mole^{-1}$ for all the ions of the surface.[38]

For the chemical behaviour of a substance, it is important that the mechanical work is used up in increasing the strength of the electron-donor properties of the anions. In the approximation being considered, the energy of chemical reactions on the disordered surface of an ionic crystal is explained by the following thermochemical cycle:

$$\begin{array}{l} Mg^{2+}O^{2-} \longrightarrow Mg^{+}O^{-} \\ O^{-} + XY \longrightarrow OX^{-} + Y \\ Mg^{+} + Y \longrightarrow Mg^{+}Y \\ \hline Mg^{2+}O^{2-} + XY \longrightarrow YMg^{+}OX^{-} \end{array}$$

where XY is a chemisorbed molecule, for example H_2, H_2O, etc. When the energy required for electron transfer (first stage) is lowered to the value of the thermal effect of the two subsequent exothermal chemical reactions, the overall reaction becomes energetically favourable.

Thus whereas in photochemistry the transfer of an electron takes place as a result of the absorption of a quantum of light, and the lifetime of the active excited state $\{Mg^{+}O^{-}\}$ is short, in mechanochemistry the ionisation is facilitated by the production of structural disorder, and the active state is metastable at room temperature.

In magnesium oxide (see Fig. 5), the ionisation energy is lowered to 4 eV. In crystals with a narrower band gap (GeO_2, SnO_2[32]), the absorption spectrum of the surface states after the production of disorder extends to the long-wave boundary of the visible range; in this case the first stage of the thermochemical cycle examined above takes place spontaneously. Similar processes are possible in organic compounds. Calculations[42] have shown that a local increase in the C–C bond in polyethylene should be

accompanied by a decrease in the ionisation potential to half its value; the transfer of an electron from the deformed bond into a structural trap then becomes possible.[43]

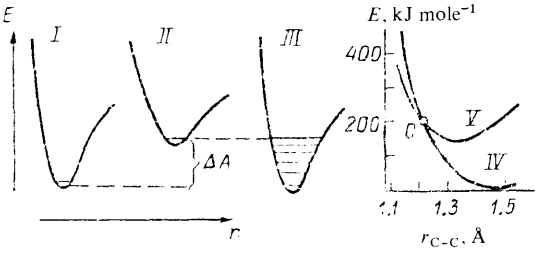


Figure 5. The relaxation of elastically deformed bonds (for explanation see text).

These examples are given here to emphasise that in the band gap of deformed ionic and covalent crystals, donor and acceptor electron levels localised on structural defects are created. These levels may be ionised thermally, and may capture biographic electrons or holes, that is electrons or holes previously existing in the crystal, including those from impurity atoms with variable valence.

The existence of easily ionisable defects is confirmed by their partial ionisation during the mechanical treatment of solids, and also by the anomalously high radiation yield for the formation of paramagnetic centres under the influence of ionising radiation on mechanically disordered crystals.[20,44] Thus after mechanical treatment and irradiation with a dose of less than 1 Mrad, 10^{17} g^{-1} F-centres are produced in radiation-stable magnesium oxide.[44] Their concentration does not increase with increase in the dose, since the vacancies are created during mechanical treatment, and irradiation leads only to their occupation by electrons.

The production of structural disorder in inorganic salts containing complex polyatomic anions should apparently increase their tendency to decompose. In fact, complex anions such as N_3^-, $C_2O_4^{2-}$, NO_3^-, etc., after the loss of an electron, are converted into a singly-charged form or a neutral species; this state is generally unstable, and the loss of the electron initiates the subsequent breakdown of the anion into individual fragments. The probability of breakdown is naturally much greater on the surface or close to defects, where there are no geometric restrictions on the formation of products.

Thus the increase in the donor properties of anions in the production of disorder must be regarded as one of the most important factors in the processes involved in the mechanical decomposition of inorganic compounds. This approach to the nature of the decomposition is confirmed by the influence of metal oxides on the extent of the mechanical degradation of nitrates.[45] This work was begun about 20 years ago, but was subsequently neglected.

III. STRUCTURAL RELAXATION

The chemical and physical effects accompanying the restoration of a mechanically disordered structure are extremely varied, and this variety is the most interesting feature of the processes involved in the deformation and breakdown of solids. The variety is due to the partial ionisation of structural defects and the existence in the deformed solid of both neutral and electrically charged centres. It is usual[2-5] to divide conditionally the entire range of phenomena into mechanochemical and mechano-emission phenomena, the former being produced by the relaxation of neutral disordered parts of the structure with the liberation of elastic energy, and the latter involving the recombination of charges and the decay of electric fields. There is obviously no distinct boundary between these overlapping groups of phenomena.

1. Excited States

In the restoration of a mechanically disordered structure, vibrational and electronic excited states are produced.[46,47] Vibrational excitation is possible as a result of the transformation of elastic energy into vibrational energy on free contraction of a previously elongated chemical bond.[46] This process is explained by Fig. 5, where *I* is the potential curve for the interaction of the atoms, *II* is the same for the elastically deformed bond, and ΔA is the work of deformation. The change *II* → *III* illustrates the relaxation of an elongated bond under conditions when no work is done against external forces. When the deformational energy liberated on bond relaxation is comparable with even half of the bond strength, the level of vibrational excitation will correspond to an effective temperature of tens of thousands of degrees. The excited bond can either undergo thermalisation (Joule heat) or take part in a chemical reaction.

The simplest example of the almost free contraction of bonds is provided by the relaxation of an elongated chain of atoms after its rupture. The model of a contracting chain has recently been the subject of computer experiments. The chain consisted of 20–100 spheres with the mass and dimensions of carbon atoms,[48] and the potential of the interaction between them was given by a Morse function. The preliminary deformation reached 0.5–1.5 Å per bond. After elongation, one end of the chain was "released" and the coordinates of all the atoms were followed. At a definite level of the excess energy, the contraction was accompanied by bond rupture. The calculated mass spectra of the fragments (for preliminary elongation of all the bonds of the chain by 1 Å) are given in Table 1.

Since the lifetime is short, the participation of vibrationally excited states in bimolecular reactions with species of the surrounding medium is less probable than monomolecular transformations such as, for example, decomposition of the substance. Decomposition is studied (see Fig. 6) by deforming or rupturing the specimens before their introduction into the mass spectrometer or chromatograph, which records the ejection of atoms of molecular fragments. The elongation and rupture of polymers gives a whole series of low-molecular compounds,[18,49,50] from hydrogen atoms to compounds containing 2–6 carbon atoms. The fracture of alkali metal halide crystals is accompanied by the ejection of neutral metal and halogen atoms,[51,52] whereas the carbonates under the same conditions decompose with the liberation of carbon dioxide,[14] the nitrates with the liberation of oxygen and oxides of nitrogen,[53] etc.[55] Not all of these effects can be fully explained by the decay of vibrationally excited states.[54]

In early studies,[51] most attention was directed to proving the existence of mechanical decomposition of the substance, and the quantity of fragments formed was not always measured. In polymers, the yield of low-molecular compounds is much lower than the number of ruptures of the

macromolecules. In the fracture of different crystals, the yield of fragments (calculated for 1 m^2 of surface formed) apparently varies from 10^{15}–10^{17} molecule m^{-2} in alkali metal halide crystals[51,52] to 10^{18}–10^{19} molecule m^{-2} in alkaline earth metal carbonates.[14] In a number of cases, the yield is possibly too high, because not all authors have taken account of the intensive sputtering of the substance in the initial period of growth of the crack; the part played by this phenomenon has been analysed.[52]

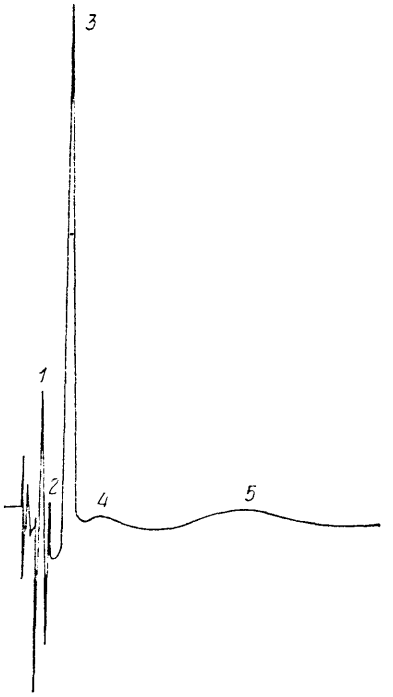
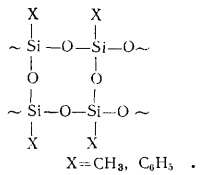


Figure 6. Chromatogram of the low-molecular products of the mechanical degradation of polypropylene: *1*) methane, *2*) ethane, *3*) propane, *4*) propylene, *5*) butane fraction.[49]

Table 1. The calculated number of fragments[48] in the free contraction of a chain of carbon atoms.

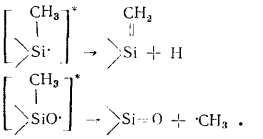
Number of C atoms in the chain	Number of C atoms in the fragment						
	1	2	3	4	5	6	7
30	4	5	1	—	1	—	1
50	6	12	1	4	—	—	—
100	14	13	7	6	4	—	1

A quantitative study of low-temperature (80 K) mechanical decomposition has been carried out for polysiloxanes with a ladder structure, namely polymethyl- and polyphenylsilasesquioxanes:[50]



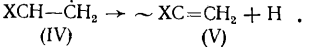
Contrary to widespread opinion, the rupture of the siloxane bonds takes place by a free-radical mechanism.[56] At 80 K, the degradation is accompanied by the ejection of hydrogen atoms and methyl radicals (for X = C_6H_5, benzene is ejected) with a probability of ~0.8, calculated for each bond rupture. As a result of secondary reactions, the H atoms and $CH_3^{\cdot}$ radicals are converted into H_2, CH_4, and C_2H_6.[50]

The primary radicals formed at the moment of rupture of the elongated polymer chain are apparently excited, and have an excess of vibrational energy; thus in spite of extensive cooling, they decompose at the β-bond with a probability close to unity:



This decomposition route is facilitated by the fact that the expenditure of energy in the rupture of the C–H and Si–C bonds is partly compensated by the gain on the formation of unsaturated groups.

The excitation of vibrations with a high amplitude changes the nature of the interaction between the atoms at the points of maximum separation from and closest approach to one another. The removal of atoms may be completed by bond rupture, and when there is appreciable approach of the carbon atoms at the end of a ruptured polymer chain, when the distance decreases to the value characteristic of a double bond, rearrangement of the atoms may take place. This situation was first analysed for the removal of a hydrogen atom from a vibrationally excited terminal radical of the type ~CHX–$\dot{C}H_2$:[57]



The potential curves (see Fig. 5) corresponding to the initial (IV) and final (V) states intersect at the point *C*. For reaction to take place, that is the transformation (IV) → (V), it is necessary that the level of excitation reach the crossing point of the potential curves.

A characteristic feature of ionic compounds is that the mechanical rupture of the bonds is preceded by the transfer of an electron from the anion to the cation.[7] This characteristic feature of ionic compounds has been used to explain the emission of neutral atoms during the fracture of alkali metal halide crystals;[58] it was assumed that in the mouth of the growing crack there is excitation of the vibrations of ions, whose amplitude is such that electron transfer from a halide ion to a metal ion takes place at the point of maximum separation from one another. Neutral atoms, which are not held by forces of electrostatic interaction, leave the surface. The results of calculations[58] showing that the emission of the atoms amounts to 10^{19} m^{-2} are too high, since for this yield, the energy used up in the sputtering of the substance is greater than the energy of breakdown; this mechanism may however make a contribution to the overall yield of the emission of atoms (see Ref. 54 for other mechanisms).

The range of mechanochemical relaxation phenomena is not restricted to the vibrational excitation of bonds. When various structural defects disappear, energy is liberated in

quantities of up to several eV, which is sufficient for electronic excitation. Under favourable conditions, the production of electronically excited states can be detected from the characteristic luminescence of the specimen. Comparatively bright mechanoluminescence (or triboluminescence) is characteristic of materials whose structures contain luminescent centres, that is luminophores. Substances in which luminescent defects are formed as a result of mechanical treatment are more interesting; examples of solids of this kind are provided by quartz[59] and copper.[60] In quartz, the luminescent structural defects are atoms with one or two broken bonds, the free radicals $\equiv SiO^{\bullet}$, and the silylene centres =Si:. The excited electronic state of the $\equiv SiO^{\bullet}$ radicals corresponds to an energy of 1.91 eV, and these radicals show luminescence in the red range of the spectrum. The silylene centres correspond to a blue luminescent band with a maximum at 2.65 eV.[59]

When fine quartz powders are subjected to mechanical treatment, the structural defects, including luminescent defects, are localised chiefly on the surface of the particles. Under these conditions, luminescence is observed when the surface is excited by ultraviolet light or friction, or by the heat of chemical reactions with gases.[59] The relaxation of residual stresses is also accompanied by luminescence. In the first studies, the excitation of triboluminescence in quartz was related to the processes involved in the disappearance of short-lived active states, for example the recombination of neighbouring radicals and the relaxation of extensively deformed siloxane bonds. The subsequent determination of the details of the electronic excitation routes encountered considerable difficulties. It was found that the contribution of processes involving the transfer of energy to the luminescence centres is small,[59] and it appears that during friction or on the relaxation of stresses, at least some of the $\equiv SiO^{\bullet}$ and =Si: centres are produced even in the electronically excited state.

Thus one of the elementary acts in the relaxation of stresses may be the reaction of a $\equiv SiO^{\bullet}$ radical with an adjacent highly deformed $\equiv Si...O...Si\equiv$ bond:

$$\equiv SiO^{\bullet} + \equiv Si..O...Si\equiv \rightarrow \equiv Si-O-Si\equiv + [\equiv SiO^{\bullet}]^{*} \ .$$

The reaction gives the electronically excited radical $[\equiv SiO^{\bullet}]^{*}$ and a non-deformed siloxane bond. Reaction (1) describes not only the production of electronically excited states but also the migration of defects with scattering of the energy, that is the development of plastic deformation.

The mechanoluminescence of copper has been observed[60] during strong impact on the end face of a metal bar; the luminescence was produced on its opposite side. Several years after the detection of the luminescence of metals, a theory was proposed, relating this phenomenon to the annihilation of edge dislocations in the volume or on the surface of the metal.[61] The energy required for the excitation of the luminescence (2.15, 1.25, and 0.85 eV) is liberated in the recombination of electrons with holes localised on the copper atoms at the centre of the edge dislocation; at these atoms there are broken bonds similar to those of free radicals at the centres of the dislocations in covalent semiconductors. The characteristic luminescence times correspond to the times taken for the dislocations to reach the surface after impact.

Thus the pictures of the build-up and quenching of the mechanoluminescence in quartz, copper, and other substances reflect the processes involved in the production, migration, and disappearance of structural defects.

2. Mechano-emission Phenomena

The emission of fast and slow electrons, including exo-emission, electrical conductivity pulses, X-rays, static electricity, gaseous discharge, and various forms of luminescence, that is a complete range of electrophysical phenomena accompanying deformation and cohesion and adhesion breakdown, are usually distinguished in the group of mechano-emission effects. Mechano-emission phenomena have been examined in comparative detail in a number of reviews, collected papers, and monographs.[1-5,9,54,55]

As noted above, the factors responsible for mechano-emission phenomena are to be found in the production, interaction, and scattering of electric charges, and one of the principal directions of research in this field still involves the interpretation of the mechanisms of the ionisation of a substance and the creation of electric fields. Several mechanisms have been discussed. The thermo- or auto-ionisation mechanism was examined above; it involves the capture of electrons (or holes) on the local levels of structural defects.

The dislocation mechanism involves charge transfer by mobile dislocations. The dislocations in crystals are electrically charged;[62,63] their charge is compensated by a cloud of charges of opposite sign, localised on point defects. During deformation and breakdown, the dislocations carry their charge on to the surface. When fracture is unsymmetrical, different parts of the crystal are deformed in different ways, and in the mouth of the growing crack there is a component of the movement of the dislocations directed towards the thicker part of the crystal; the excess charge is carried with the dislocations. In alkali metal halide crystals, the excess charge reaches $10^{5}-10^{7}$ CGSE unit m^{-2} or $10^{14}-10^{16}$ centre m^{-2}. In this case the results of calculations[64] agree with the results of measurements of the magnitude of the charge.[65]

The polarisation mechanism is the simplest to explain. The electric fields are produced in this case as a result of the orientation of the polar molecules during the development of the deformation; a similar effect is observed when there is a relative displacement of ions of opposite charge. Thus for identical orientation of all the side groups of polymethyl methacrylate, the charge density would be 9×10^{7} CGSE unit m^{-2}; the experimental value is approximately 10 times smaller, 6×10^{6} CGSE unit m^{-2}. The polarisation mechanism plays the principal role in the production of electrets in polymers;[66] an appreciable polarisation EMF is produced when shock waves pass through a substance.[67]

The mechanism of the separation of the electrical double layer is characteristic of the breakdown of adhesion contact. An electrical double layer is always produced at the boundary of contact between two surfaces of different kinds, and from this viewpoint the breakdown of adhesion contact is identical to the separation of the plates of a capacitor.[9] The charges produced when a polymer film is torn from a support, or when plates of mica are split, represent the most familiar examples of the consequences of electrification by this mechanism.

The production of electric fields during the deformation or breakdown of solids is usually accompanied by scattering of the excess charge. The charged centres preserved after mechanical treatment are responsible for post-effects—a decrease in electrical conductivity, the emission of electrons or ions, and luminescence excited by the recombination of charges.[68] These processes are completed with increase in temperature (exo-emission, thermoluminescence) and by the adsorption of gases and vapours on the surface.[69]

In the deformation and breakdown of solids in air or in another gas atmosphere, the principal route for the scattering of the charges is by electrical breakdown, that is gaseous discharge accompanied by characteristic luminescence, acoustic effects, etc. In a vacuum, the charges may be scattered in several ways. When the electron is firmly bound to a centre, for example to a structural defect, the decisive factor in the scattering of charges is the stability or mobility of the defects themselves. Thus in polymers, electrons may be stabilised in so-called structural traps or vacancies. On deformation or with increase in temperature, the structural traps are destroyed, with the liberation of electrons and the excitation of emission, conductivity, or recombination luminescence.[43] Processes of this type include the capture of *F*-centres by moving dislocations with subsequent recombination of charges. In the other limiting case, when the concentration of charges is high, and the electrons are not so firmly bound to the traps, the principal role in the relaxation of charges is played by the emission of electrons, brought about by their repulsion from one another. The intensity of the emission of electrons in a vacuum is determined by the fluctuations in the surface charge density; for a local charge density of 10^8 CGSE unit m^{-2}, the energy of the emitting electrons may reach 10^1–10^2 keV.[54,68]

A radiation mechanism of charge scattering has been proposed to explain the mechano-emission effects accompanying the splitting of alkali metal halide crystals.[54] The electrically charged walls of the growing crack represent a rapidly separating capacitor, in the field of which the velocity of the electrons and ions leaving the surface is increased. The accelerated particles bombard the opposite wall of the crack, producing excitons; some of the excitons decay with the ejection of a free cation. The cation is accelerated by the field of the capacitor, bombards the opposite wall of the crack, etc. The consequences of the individual stages, that is the emission of accelerated electrons (Deryagin effect), exciton luminescence, the emission of excited cations, and the appearance of radiation defects on the walls of the crack, have been detected by various methods.[51,52,70,71]

IV. DEFORMATIONAL MOBILITY AND THE KINETICS OF DIFFUSION-CONTROLLED REACTIONS

During the deformation of solids, different forms of mobility are excited. These include both the usual forms of thermal motion, but mechanically activated, and also purely mechanical deformational mobility. In the first case, the mobility is clearly activational in character, and the movement of particles requires that an energy barrier be overcome. In the second case, the motion is practically athermal, and the contribution of thermal fluctuations to the mobility is negligible compared with the role of internal stresses. The movement of dislocations and grain boundaries can be classified as deformational mobility.

Familiar examples of the mechanical activation of thermal motion include ascending diffusion, diffusion creep, diffusion along dislocations, etc. The role of super-equilibrium defects in activated diffusion has been less extensively studied. For the vacancy mechanism, the diffusion coefficient is directly proportional to the concentration of vacancies. For many materials at room temperature this is negligible, but it may be increased sharply by mechanical treatment, reaching 10^{16}–10^{17} g^{-1}.[20,44] The diffusion coefficient is also increased by many powers of ten. This effect is apparently important for the mechanical activation of sintering processes.

At a concentration of vacancies of ~10^{17} g^{-1}, a solid is saturated by defects to almost the same extent as on fusion, when there is one vacant site for every 10^3–10^4 atoms in lattice sites. This state differs from fusion in that it is produced at a comparatively low temperature, when jump-over by the atoms is difficult. As the deformation develops, however, this restriction is removed, since the internal stresses lower the barrier to jump-over. Thus the state of a substance at the moment of intensive deformation can be represented as "cold fusion". This terminology is already encountered in the literature.[72]

The mechanical mobility of a structure should also be revealed in the kinetics of chemical reactions. The relationship between reaction rate and molecular mobility is one of the basic characteristic features of chemical reactions in solids. The mobility produced by internal stresses is no exception to this rule.

A convenient system for the study of the mobility of a structure subjected to different mechanical treatments may be provided by diffusion-controlled completely frozen reactions between particles which are distributed in a solid matrix and which do not react with one another only because of the absence of mobility. These processes include so-called static reactions between adjacent particles, for example between radicals in pairs or between a radical and a neighbouring molecule of the matrix, and also reactions between particles situated at an appreciable distance from one another, for example the recombination of radicals or charged centres. It has been established experimentally that reactions of both types are much more intensive in a deformed material.[72–76]

To determine how the rate of a chemical reaction is related to the development of deformation, and to estimate the work done in bringing about a reaction, quasi-monomolecular statistical reactions and bimolecular diffusion-controlled reactions in systems with frozen translational mobility are examined separately below.

1. Statistical Pseudo-monomolecular Reactions

The mechanical intensification of reactions between adjacent particles has been observed in dilute frozen solutions of polymers at 80 K.[73] Mechanical treatment was accompanied by degradation of the macromolecules P with the formation of radicals $R^{\bullet}$ and their secondary reactions with molecules of the matrix: hydrogen atom donors HX or the monomer M:

$$P \rightarrow R^{\bullet} \qquad (2)$$

$$R^{\bullet} + HX \rightarrow RH + X^{\bullet} \qquad (3a)$$

$$R^{\bullet} + M \rightarrow RM^{\bullet} \ . \qquad (3b)$$

The extent of the transformation in replacement (3a) or addition (3b) reactions was followed by EPR. Fig. 7*a* shows the changes in the concentration of the radicals $R^{\bullet}$ (curve *1*) and $RM^{\bullet}$ (curve *2*) and the total concentration $R^{\bullet} + RM^{\bullet}$ (curve *3*). On prolonged mechanical treatment of the specimens, reactions (3a) and (3b) were accompanied by the disappearance of the radicals, and when this process stopped, the reactions stopped. The curves giving the change in the concentrations of the radicals $R^{\bullet}$, $RX^{\bullet}$, or $RM^{\bullet}$ during the mechanical treatment of the powders were used to calculate the rates of the free-radical replacement and addition reactions at 80 K. The rates of most of the addition reactions studied corresponded, to within a factor of 10–100, to the value extrapolated to 80 K using the Arrhenius equation with the parameters k_0 and E characteristic of the liquid phase. The method involving the

mechanical treatment of frozen solutions has been used to compare the reactivities of various radicals and molecules at low temperatures.[73]

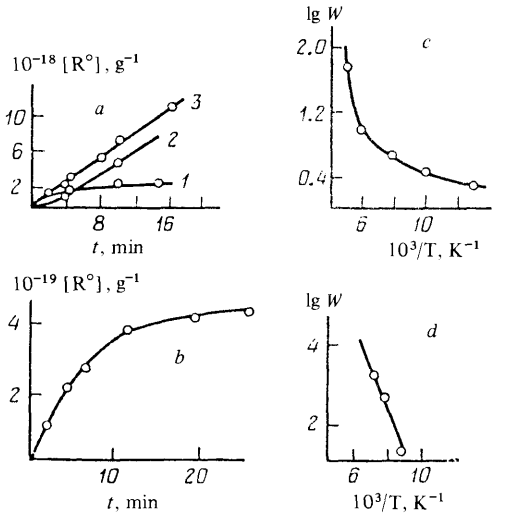


Figure 7. Free-radical reactions during the mechanical treatment of polymers (*b*) and their solid solutions (*a*, *c*, *d*);[73,77,81] rate of supply of mechanical energy in the range 1–10 W g^{-1}; *a*) addition of $\sim CH_2\dot{C}(CH_3)COOCH_3$ radicals to tetrachlorobenzoquinone at 80 K; *b*) formation and disappearance of free radicals in polystyrene at 80 K; *c*) replacement $R^{\bullet} + CH_2(COOH)_2 \rightarrow RH + \dot{C}H(COOH)_2$; *d*) addition $R^{\bullet} + CH_2{=}CH(C_6H_5) \rightarrow R{-}CH_2\dot{C}H(C_6H_5)$.

As an illustration, Fig. 7 compares the results of measurements of the rates (w) of mechanically intensified reactions involving the transfer of a hydrogen atom and addition (Fig. 7*d*) over a wide temperature range.[59] The temperature coefficient of the addition reaction in the frozen solutions is close to the activation energy of this reaction in the liquid phase (Fig. 7*d*). For the replacement reaction (Fig. 7*c*), the Arrhenius law is not observed, since at a low temperature, the transfer of a hydrogen atom takes place by a tunnelling mechanism.

A rigorous description of the kinetics of mechanically intensified random reactions was recently carried out[78] using the concept of the mechanical movement of kinetically non-uniform systems in which there is a wide distribution of reaction centres with respect to reaction rate constants. In solids at a low temperature, when the mobility is frozen, the non-uniformity is due to differences in the nature of the immediate environment of the particles.[79]

Under ordinary conditions, the relative arrangement of the particles remains unchanged during the reaction, and the function $n(k)$ characterising the distribution of the particles with respect to the rate constants remains constant; the reaction leads to gradual "burn-out" of the fractions of the distribution with rate constants close to the maximum value k_{max}. Deformation influences the structure of the immediate environment of the particles and displaces the reaction system, restoring the burnt-out "rapid" fractions. As a result, a varying distribution of the particles with respect to rate constants $n(k, t)$ is established, depending on the frequency of the mechanical displacement ν and the time t.

The number of particles in an arbitrarily selected fraction of the current distribution with respect to rate constants $n(k, t)$ is determined by the ratio of the rates of three processes:[78]

$$\frac{d}{dt}\{n(k, t)\} = -kn(k, t)\,dk - \nu n(k, t)\,dk + \nu N(t)\,\frac{n(k, 0)\,dk}{N(t)} \quad .$$

The first two terms characterise respectively the loss of particles from the fraction as a result of the reaction with rate constant k and mechanical displacement with frequency ν. The third term describes the replenishment of the fraction k as a result of a redistribution of the particles from other fractions on mechanical displacement: of the total flux $\nu N(t)$, where $N(t)$ is the current concentration of particles, only the fraction $n(k)dk/N(t)$ corresponding to the contribution of this fraction to the current concentration $N(t)$ enters the fraction k.

Under conditions of intensive displacement, the current distribution function $n(k, t)$ does not differ greatly from the original function $n(k)$, since for $\nu \ll k_{max}$ the loss of the rapidly burnt-out fractions is immediately made good by replacement; the rate of the process is therefore described by the equation for a first-order reaction

$$-\frac{dN(t)}{dt} \approx k_{max}\frac{N(t)}{\ln(k_{max}/k_{min})}$$

but the effective concentration is lower than the total concentration by a factor of $[\ln(k_{max}/k_{min})]^{-1}$. The factor $[\ln(k_{max}/k_{min})]^{-1}$, determined by the width of the hyperbolic distribution of the particles with respect to rate constants,[80] takes account of the fact that the reaction develops only as a result of the particles in that part of the distribution adjoining k_{max}. In other words, in spite of strong displacement, the reaction rate remains slower than the maximum possible.

Thus intensive mechanical displacement moves a slow reaction, retarded because of the absence of mobility, into conditions close to kinetic. On less intense mechanical treatment, or in a reaction system with high values of k_{max}, when $k_{max} > \nu > k_{min}$, the observed rate constants are determined by the frequency of the displacement:[78]

$$-\frac{dN(t)}{dt} = \nu\frac{\ln(k_{max}/\nu)}{\ln(\nu/k_{min})}N(t) \quad .$$

2. Bimolecular Reactions

The displacements of structural elements, associated with the development of a deformation, through distances which are large compared with the lattice parameters can readily be detected from the intensification of reactions involving the recombination of radicals (by EPR) or charged centres (from the luminescence). Bimolecular reactions of this type have been observed during the mechanical treatment of polymer powders in mills,[73,74,81,82] during the plastic deformation of substances on Bridgman anvils,[6,11,12] during the monoaxial elongation of polymer films,[75,76] in the shear deformation of alkali metal halide crystals,[83] and in other systems.

The limit of the accumulation of active centres during the mechanical treatment of solids is related to deformational recombination. This phenomenon has been detected during the subdivision of polymer and quartz powders, and its essential feature is that the number of free radicals at first increases according to a linear law, but after some time their

accumulation stops, in spite of the fact that the mechanical degradation continues at a constant rate[74] (see Fig. 7*b*). During fine subdivision, work is done chiefly to deform the shape of the particles of the powder and in friction. For polymers, for which the yield stress is low ($\sim 10^7$ N m^{-2}), even under comparatively mild dispersal conditions, for an energy intensity of 0.1–1.0 J g^{-1} s^{-1}, bulk deformation conditions are produced, that is the mechanochemical transformations are due chiefly to plastic deformation of the particles, and not to their splitting or to friction against one another.

For solid quartz powders under the same conditions, friction takes place.[26] The deformation is localised in a thin layer of the particles next to the surface, and all the active centres are concentrated on the surface and accessible to molecules from the gas phase. For solid materials, the change from surface deformation (friction) conditions to bulk deformation conditions is possible when there is a decrease in the particle size[46] or a sharp increase in the energy intensity.[84]

Bulk and surface deformations lead to the rupture of chemical bonds and the migration of radicals, and hence to their encounter and disappearance. Migration may be due either to the direct displacement of the structural elements with localised active centres or to the breakdown of macroradicals with the subsequent diffusion of low-molecular fragments, or to various relay mechanisms, such as the gliding of dislocations or the displacement of free-radical states to the quartz surface according to scheme (1).

Thus the current concentration of defects such as radicals or other active centres during mechanical treatment is determined by the competition between the processes of their formation and disappearance.

The formation of defects is characterised by the magnitude of the energy yield $G_M(R^\bullet)$, which is determined from the slope of the initial section of the accumulation curve (see Fig. 7*b*). On the stationary section, where the concentration of defects is equal to the limiting concentration $[R^\bullet]_\infty$, the energy yields for their formation $G_M(R^\bullet)$ and disappearance $G_M(-R^\bullet)$ are equal to one another.

Table 2. The energy yield and the limiting concentrations of free radicals during the mechanical treatment of powdered polyethylene and quartz (calculated from published data[15,74,81]).

Substance	Degradation conditions	G_M, mole MJ^{-1}	$[R^\bullet]_\infty$	σ, N m^{-2}
Polyethylene	volume deformation	$\sim 10^{-3}$	~ 10 mole m^{-3}	$\sim 10^7$
Quartz	friction	$\sim 10^{-3}$	$\sim 10^{-7}$ mole m^{-3}	10^9–10^{10}

The values of the parameters $G_M(R^\bullet)$ (to within an order of magnitude) and $[R^\bullet]_\infty$, characterising the processes involved in the formation and disappearance of radicals during the mechanical treatment of polyethylene and quartz in a vibration mill (intensity ~1 W g^{-1}), are given in Table 2. Unfortunately, these parameters cannot be estimated for other materials, since the appropriate papers do not give the expenditure of mechanical energy.

Plastic deformation may be homogeneous and cover the entire volume of the substance. The softer the material and the greater the load, apparently, the closer the dynamics of mechanochemical transformations are to this homogeneous model. Much more frequently, however, plastic deformations develop in local zones: in the glide planes of dislocations, in the layers between crystallites, in shear bands, etc. The micro-heterogeneity of the development of deformation is clearly revealed in the processes involved in the disappearance of radiation defects as a result of deformation. Thus when there is appreciable shear deformation of γ-irradiated alkali metal halide crystals, only 5–10% of the defects, situated in the glide planes of the dislocations, disappear.[83] During the monoaxial elongation of polymer films, ~50% of the radiation-induced radicals disappear.[75] In the binary systems hydrocarbon–halogen, etc., γ-irradiated at a low temperature, slight initial deformation initiates a chain reaction covering ~1/4 of the volume of the substance;[85,86] the chain process apparently develops according to the following scheme: deformation–reaction with a change in volume–shrinkage deformation–reaction etc.

Displacement within the entire volume of a substance at the molecular level has been observed during the mechanical treatment of powders in mills, where the particles are subjected to repeated impact. Under these conditions, practically all the radicals produced by γ-irradiation in polymers disappear,[78] but the mechanochemical reaction of metals with halogens, sulphur, selenium, or tellurium takes place explosively.[87]

The nature of the relationship between deformation and the yield of a bimolecular reaction depends on the mechanisms of the development of the deformation and the migration of the reaction centres. The dynamics of the development of a reaction in the glide plane of dislocations can be considered first: a geometric model of the process is shown in Fig. 8*a*. Moving from left to right, the dislocation covers all the reaction centres in the glide plane, and they react with one another in a narrow zone close to its centre.

The change in the concentration of reaction centres on the dislocation line (n_L, m^{-1}) as it moves in the direction x is given by the relationship

$$\frac{dn_L}{dx} = (1 - r_0 n_L) n_s - r_0 n_L n_s$$

where r_0 is the capture cross-section radius, and n_S the concentration of centres in the glide plane of the dislocation, m^{-2}. In all cases, $n_L = bn_S$ and $n_S = bn$, where b is the lattice parameter, and n the volume concentration of reaction centres, m^{-3}. For $L = 1$, the product $r_0 n_L$ characterises the degree of filling of the dislocation line by reaction centres, the first term corresponds to the fraction of centres captured on the free sections of the dislocation line, and the second term corresponds to the number of collisions leading to reaction and the liberation of centres from the dislocation line. The expression for the current concentration of centres on the moving dislocation line has the form:

$$n_L(x) = \frac{1}{2r_0}\{1 - \exp(-2r_0 n_s x)\} + n_0 \exp(-2r_0 n_s x) .$$

The number of centres disappearing on collision with a dislocation is given by

$$-dn_L = 2r_0 n_L(x) n_s dx .$$

Substituting the function $n_L(x)$ and integrating gives

$$\Delta n = n_s x - \frac{1}{2} n_\infty \{1 - \exp(-2r_0 n_s x)\} .$$

This equation describes the development of the bimolecular reaction in the glide plane of a dislocation. Initially, in the acceleration section, the reaction centres accumulate on the

dislocation line; after the limiting concentration of centres $n_{\infty,L}$ (equal to half the number of positions on the dislocation line) has been reached, stationary reaction conditions are established, when all the centres appearing react immediately. The distance x_{cr} at which the change in conditions takes place is $x_{cr} \cong n_{\infty,L}/n_s$. When the critical mean free path is greater than the average distance between dislocations, the most favourable conditions for the reaction, for which $\Delta n \cong n_s x$, cannot be established, since the dislocations will arrive too early at an area free from reaction centres.

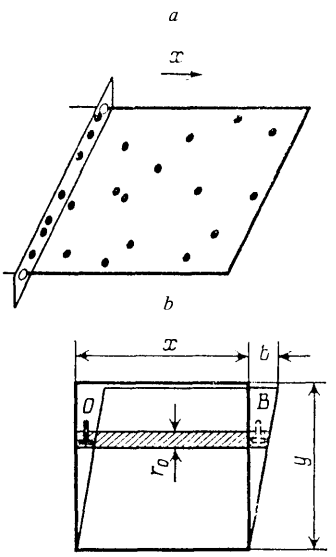


Figure 8. Diagrams explaining the development of a bimolecular reaction in the glide plane of a dislocation (for explanation see text).

To estimate the energy yield of a bimolecular reaction stimulated by the movement of dislocations, Fig. 8*b* can be considered. The volume V corresponding on the average to one dislocation and equal to $V = xy : 1$, is outlined by the continuous line in Fig. 8*b*. Under the influence of the shear stress σ, the dislocation is displaced from the position O to the position B, at the boundary of the volume V, which is equivalent to a displacement of all the substance above the glide plane by an amount equal to the lattice parameter b. The relative deformation ε is then given by $\varepsilon = b/y$. The work A done by the shear force in the path b is equal to $A = \sigma b x . 1$, and the number of particles Δn reacting in the path x in the glide plane of the dislocation is equal to $\Delta n = n r_0 x . 1$. Since the path x is the average distance between the dislocations in the glide plane, paths whose length is greater than x will be "superfluous". Under the most favourable conditions, the energy yield of the reaction G_M is given by the expression:

$$G_M = \frac{\Delta n}{A} = \frac{r_0 n}{b\sigma} \quad \text{or} \quad G_M \simeq \frac{n}{\sigma_y} \ .$$

In the last relationship it is assumed that $r_0 \cong b$, and that the stress σ is close to the yield stress σ_y.

For $\sigma_y \cong 10^7$ N m^{-2} and $n = 10^2$–10^3 mole m^{-3} (which corresponds to a number of centres ~10^{20} cm^{-3}), the energy yield may reach 10–100 mole MJ^{-1}, that is in the example being considered, the work done in carrying out the reaction should be comparable with the heat required to fuse the reaction system.

The energy yield of the reaction when the deformation develops by a slip mechanism can be estimated similarly. When the atom planes slip relative to one another, the particles of one plane encounter particles situated in the other. To a first approximation it can be assumed that for a relative displacement of the planes through a distance Δl, the number of reacting particles in unit area is given by:

$$\Delta n_s = r_0 \Delta l n_s^2 \quad \text{or} \quad \Delta n = r_0 b \Delta l n^2 \ .$$

The work A done in the displacement of the planes relative to one another is equal to $A = \sigma \Delta / b$, and the energy yield of the reaction $GM(-R^{\bullet})$ is given by

$$G_M(-R^{\bullet}) = \frac{\Delta n}{A} = \frac{V_0}{\sigma} n^2 \ .$$

Here, the product $r_0 b^2$ is taken as equal to the reaction volume V_0. In contrast to the dislocation mechanism, in the case of the slip mechanism the energy yield is directly proportional to the square of the concentration of centres. A similar relationship will be observed when there is external friction:

$$G_{fr}(-R^{\bullet}) = \frac{r_0}{\sigma_{fr}} n_s^2 \ .$$

Here, the tangential stress σ_{fr} is equal to $\sigma_{fr} = \mu p$, where μ is the coefficient of friction, and p the normal pressure.

In internal and external friction, the free radicals are formed at the point of rupture of the bonds and disappear. Under stationary conditions, the yields of the formation $G_M(R^{\bullet})$ and disappearance $G_M(-R^{\bullet})$ of radicals are equal to one another, and the concentration is equal to the limiting value $[R^{\bullet}]_{\infty}$. Since for polyethylene and quartz, $G_M(R^{\bullet})$ and $[R^{\bullet}]_{\infty}$ are known (see Table 2), it is possible to estimate the magnitude of the tangential stresses under the conditions of the mechanical treatment of the powders. The results of the estimates are given in the last column of Table 2. In the calculations it was assumed that $r_0 \cong 3 \times 10^{14}$ m mole^{-1}, and $V_0 \cong 1 \times 10^4$ m^3 mole^{-1}. In polyethylene, the stresses are of the same order of magnitude as the yield stress (10^7 N m^{-2}), whereas in quartz they are 10^2–10^3 times greater.

Under real conditions, the energy yield may be influenced by several factors. In the first place, the probability of the reaction when the particles meet may be less than unity. Next, to complete the reaction it is necessary to have plastic deformation of the entire volume of the crystal, and not merely the regions adjoining the glide planes, so that the stresses should be much greater than the yield stress. Finally, under real conditions it is difficult to avoid superfluous displacement of the dislocations, and superfluous deformation. Nevertheless, deformation recombination provides a convenient and informative method for studying the processes involved in the development of deformation; the first studies in this direction have already been carried out.[83]

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Mechanical stresses, like ionising radiation and other physical methods of acting on a substance, initiate and accelerate chemical reactions. In photochemistry and in radiation chemistry, the energy quanta interacting with a

substance are comparable to or greater than the strength of the chemical bonds, so that the chemical action of the radiation is natural. In mechanochemistry, on the other hand, the average level of the elastic potential is usually very low, and the possibility of the production of chemical effects is not always obvious; it is therefore necessary to assume that mechanisms for concentrating the energy exist. One of the principal ways in which the elastic energy can be concentrated is by the formation of structural defects.

The production of vacancies and interstitial atoms, dislocations, and internal and external surfaces of separation by various treatments reflect a general tendency shown by crystals to transform energy supplied from outside into the energy of crystal lattice defects. On thermal treatment, Frenkel defects are stabilised in crystals; the energy used in their formation is compensated by the increase in the configurational entropy of the crystal when vacancies and (or) interstitial atoms are produced in its volume.

In exactly the same way, in the elastic deformation of a crystal, the state of the crystal in which the dislocations or other defects at which the excess energy is concentrated are distributed in the volume is theremodynamically more favourable than the state in which there is a uniform distribution of the elastic stresses throughout all the interatomic bonds. The stabilising factor in this case also is the contribution of the configurational entropy S_c to the free energy of the crystal. Since $S_c = k \ln W_D$ (where W_D is the thermodynamic probability of the crystal with defects, equal to the number of ways in which these defects can be arranged in the lattice sites), the increase in free energy on production of the defects is given by:

$$\Delta F = F_D - F_0 = -kT \ln W_D .$$

Here, F_0 is the free energy of the elastically deformed crystal, and F_D the same for a crystal in which all the energy of deformation is concentrated in structural defects.

Thus the tendency for the excess energy to be concentrated in structural defects is a characteristic feature of the crystalline state of a substance. The nature of mechanochemical transformations is to a considerable extent related to this characteristic feature of solids.

It follows from the experience gained in mechanochemistry, and partly reflected in the present review, that the production of defects and the subsequent production of structural disorder are unavoidably accompanied by a perturbation of the electronic sub-system of a substance, ionisation, various relaxation processes, and excitation of the mobility of the structure; this provides the means by which mechanical stresses have an effective action on the reactivity of solids.

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Institute of Chemical Physics,
Academy of Sciences of the USSR,
Moscow

Translated from *Uspekhi Khimii*, 53, 1790-1826 (1984) U.D.C. 620.193.013 : 669

Regular Kinetic Features of the Dissolution of Metal Oxides in Acidic Media

I.G.Gorichev and N.A.Kipriyanov

A comparative analysis of experimental data and theories interpreting the regular kinetic features of the dissolution of metal oxides in acids has been carried out. Theories of the conjugated transfer of the cations and anions of the oxide to the electrolyte solution do not explain the results obtained. The regular kinetic features of the dissolution of oxide phases have been interpreted for the first time on the basis of the present-day theory of semiconductors, electrochemical concepts, and models of heterogeneous kinetics. The proposed electron-proton mechanism explains all the available data on the kinetics of the dissolution of oxides in mineral acids and complexones.
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I. INTRODUCTION

The intensification and optimisation of the processes involved in the etching of metals, the extraction and concentration of ores, and the removal of deposits from thermal power engineering equipment represent an important scientific and technical problem, requiring a knowledge of the mechanisms of these processes. In the present review, the complex character of the dissolution processes is demonstrated for the case of the reaction of metal oxides with aqueous solutions of various acids, for which the data on the kinetics and mechanism have not yet been adequately reviewed. A deeper analysis of the regular kinetic relationships obtained has been carried out using present-day electrochemical concepts, the zone theory of oxides, and heterogeneous models of the dissolution of oxide phases in acidic media.

The kinetics of the dissolution of metal oxides in electrolytes is influenced by the physicochemical properties of both the semiconducting oxides (the degree of covalent character of the bond, the presence of defects in the crystal lattice, the concentration of alloying additives, the crystallographic orientation of the active surface of the crystal, the nature of the active centres, the specific features of the surface states, which differ considerably from the states in the volume of the solid phase) and the solutions (concentration, pH, redox potential, presence of complex-forming reagents).

The existing reviews on this topic[1-16] do not cover the sources completely. An exhaustive analysis of data on the influence of ionising radiation on the kinetics of the dissolution of solids has been carried out.[5,17] The present review systematises the theoretical aspects of the kinetics of the dissolution of oxide phases. Electrochemical concepts have been used to explain many kinetic parameters (the order of the reaction with respect to different ions of the electrolyte), and the influence of oxidising agents, reducing agents, complex-forming reagents, and the adsorption of protons. For the quantitative calculation of the kinetic parameters of dissolution, the experimental data have been treated using present-day theories of the kinetics of heterogeneous processes. It has been shown that morphological models not only make it possible to take account of the change with time in the surface area of the dissolving oxide, but also help to explain the comparatively high activation energy of the dissolution of oxide phases in acids.

II. ANALYSIS OF THE KINETIC CURVES FOR THE DISSOLUTION OF METAL OXIDES IN ACIDIC MEDIA

1. Form of the kinetic curves. The typical form of the curves for the dissolution of powdered oxide specimens as the plots of the fraction of the dissolved substance α against the time t is shown in Fig.1. In the general case, the rate of dissolution $\partial\alpha/\partial t$ passes through a maximum (at $\alpha \cong 0.5$ to 0.7).[2,18-20] The section corresponding to the decrease in the rate of dissolution is difficult to analyse, since it depends to a marked extent on the characteristic features of the size distribution of the particles at this stage of the process.

2. Analysis of the curves for the dissolution of metal oxides in acids on the basis of affine transformations. The method of affine transformations[9,21,22] makes it pcssible to determine whether changes in the mechanism (stages) of a process are due to a particular factor influencing the rate of dissolution. If the kinetic curves corresponding to different values of any parameter are reduced to a single scale relative to the time $t/t_{0.5}$ (Fig.2), the sequence of stages in the dissolution process is assumed to be always the same from the start to the end of the reaction; the rate of the process is limited by a single stage, and not by several stages. This makes it possible to represent the rate of dissolution ($\partial\alpha/\partial t$) in the form of a function with separable variables

$$\partial\alpha/\partial t = f(T, a_{H^+}, E) \cdot f(\alpha) \qquad (1)$$

where $f(T, a_{H^+}, E) = (\partial\alpha/\partial t)_{sp}$ is the specific rate of dissolution corresponding to unit surface area of the specimen; and $f(\alpha)$ is a function reflecting the nature of the change in

the surface area of the specimen in this process. Change in the variables, T, E, and a_{H^+} influences the time taken to reach a definite fraction (α) of dissolved oxide, whereas the morphology of the surface of the specimen remains unchanged for different successive values of α.[21]

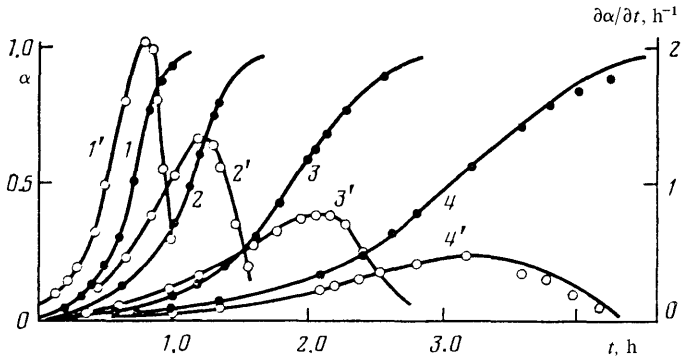


Figure 1. Time dependence of the fraction (α) of dissolved oxide CuO (*1*–*4*) and the specific rate $\partial\alpha/\partial t$ (*1'*–*4'*) of the dissolution of this oxide in aqueous H_2SO_4 solutions with different pH values at an electrolyte temperature of 25 °C; *1*) 0.43 (k_i = 7.37 h^{-1}); *2*) 0.65 (k_i = 3.65 h^{-1}); *3*) 0.85 (k_i = 2.14 h^{-1}); *4*) 1.05 (k_i = 1.34 h^{-1}). Points—experiment; lines—calculation using Eqn.(52), where $A = 0.022$.[166]

3. The theory of the specific rate of dissolution of oxide phases proposed by Nernst. In the literature up to the present, the specific rate of dissolution of crystals (1) has been calculated using the mathematical expression proposed by Nernst and Noyes.[23] The unsatisfactory features of the calculation of the specific rate of dissolution using Nernst's theory can be demonstrated. It follows from Nernst's theory[23] that the diffusion of the ions in the boundary layer of an electrolyte at the surface of separation with an oxide is the limiting stage of the dissolution of the solid

$$(\partial\alpha/\partial t)_{sp} = D(c_{sat} - c)/V \cdot \delta = k_1(1-\alpha) \qquad (2)$$

where D is the diffusion coefficient of the ions, c the concentration of the salt in the volume, c_{sat} the concentration of the salt in the saturated solution, V the volume of solution, and δ the thickness of the electrical double layer. Since Eqn.(2) does not make possible a complete description of all the regular kinetic features of dissolution, use is made of an expression of the form

$$(\partial\alpha/\partial t)_{sp} = k_2(c_{sat} - c)^n \qquad (3)$$

where n and k_2 are independent of the hydrodynamic conditions. According to Eqn.(3), the driving force of the dissolution is the difference between the salt concentrations ($c_{sat} - c$).

The unsatisfactory features of Eqns.(2) and (3) include the fact that they cannot explain the high value of the activation energy (65–85 kJ $mole^{-1}$). For a process taking place in the diffusion range, its value is 15–20 kJ $mole^{-1}$. In practice, Eqns.(2) and (3) are applicable in rare instances, since the values of k_1 and k_2 depend on the dissolution time and on the states of the volume and surface phases. Eqns. (2) and (3) describe the distribution of the concentration of the dissolved substance at a definite distance from the boundary of the solid phase, but they do not reflect the changes in concentration with time.[2] The data in Ref.24 were obtained with vigorous stirring of the electrolyte, when further increase in the rate of movement of the particles had no influence on their rate of dissolution; under these conditions, the equation of diffusion kinetics is not applicable. Kabai[24–27] modified Eqns.(1) and (3) and obtained the expression

$$\alpha = c/c_\infty = 1 - \exp[-(kt)^\gamma] \qquad (4)$$

where γ is a constant which depends on the nature of the system. Detailed verification of Eqn.(4) shows that it is inapplicable even for $\gamma = 1$.

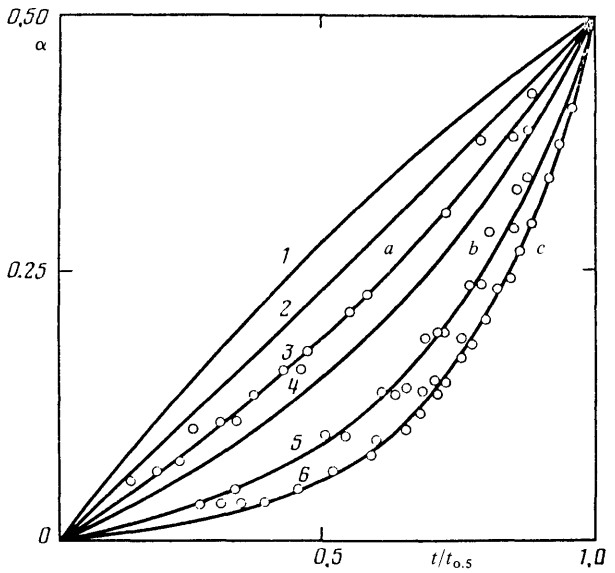


Figure 2. Dependence of the fraction of dissolved magnetite on the reduced time $t/t_{0.5}$ in aqueous solutions of H_3PO_4 (*a*), EDTA (*b*), and HEDP (*c*) under different experimental conditions (concentration, temperature, pH). Lines—calculation using Eqn.(52) for different values of A: *1*) $A = 10$; *2*) $A = 0.45$; *3*) $A = 0.20$; *4*) $A = 0.10$; *5*) $A = 0.025$; *6*) $A = 0.010$. Points—experimental data for different experimental conditions.

In the early nineteen-fifties, experimental data were obtained,[2] showing that these ideas cannot be used to describe the regular kinetic features of the dissolution of metal oxides, since analysis of the dependence of the specific rate of dissolution of oxide phases in acids on various factors established that it is determined by the concentration gradients of the protons and electrons (potential) and the stoichiometric composition of the solid phase, and this is not reflected in Eqns.(2) and (3). An explicit mathematical expression describing the specific rate of dissolution of oxides has not yet been found.

III. THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER AT THE OXIDE/ELECTROLYTE BOUNDARY AND THE DISTRIBUTION OF CHARGE AND POTENTIAL IN IT

In the dissolution of non-stoichiometric oxides (wustite, magnetite, uraninite, cobalt(II) oxide, pyrolusite, nickel(II) oxide, tenorite, and other oxides), the rate of the process depends on the potentil difference (Fig.3), since this process is determined by the rate of the transfer of ions through the electrical double layer.[2,3,28,29] It is possible to distinguish increases in the rate of dissolution due to the reduction (MnO, Mn_2O_3, MnO_2, Fe_2O_3, Fe_3O_4, FeO) and due to the oxidation (NiO, Cu_2O, UO_2) of the surface layers of the oxides.[2,3,30,31]

1. Nature of the Potential at the Oxide/Solution Boundary

When an oxide is brought into contact with a solution, an electrical double layer is produced at the oxide/electrolyte boundary (Fig.4). The total decrease in the potential (E) relative to the potential of the corresponding reference electrode (E^0) is given by

$$E=E_{sc}+E_H+E_{el}+E^0$$

where E_{SC} is the value of the potential in the volume zone of the oxide, and E_H and E_{el} the decrease in the potential in the Helmholtz layer and in the electrolyte respectively.[32] Regions of volume charge are produced on both sides of the boundary.[32] The equivalent scheme of the boundary is represented by three condensers connected in series.[33] The production of the volume charge in the oxide when it is brought into contact with the electrolyte is due to the insertion of protons (hydroxide groups) into the solid phase.[34] The charge density in this oxide is much lower than that in the metal.[33,35] Thus the potential jump between the phases[33] is concentrated almost entirely in the solid phase, and the contribution made to it by the Helmholtz layer is usually negligible.[35,36]

The magnitude and distribution of the charges and potentials are calculated using two fundamental relationships:

1) the Poisson equation

$$d^2E/dr^2=-\rho/\varepsilon\varepsilon_0 \qquad (5)$$

where ρ is the charge density (made up of both mobile charges, that is electrons $n(r)$ and holes $p(r)$, and stationary charges, that is ionised donors (N_D) and acceptors (N_A), that is $\rho(r) = e[-n(r) + p(r) - N_D + N_A]$); and ε and ε_0 are the dielectric constants of the specimen and a vacuum respectively;

2) the Gauss equation

$$dE/dr=-Q/\varepsilon\varepsilon_0 \qquad (6)$$

where Q is the density of the surface charges. It follows from Eqns.(5) and (6) that the value of the potential in the three regions will be given by the expression (see Fig.4)

$$E=\varepsilon_{sc}r_{sc}+\varepsilon_H r_H+\varepsilon_{el}\varkappa^{-1}$$

where ε_{SC}, ε_H, and ε_{el} are the electric field intensities in the region of the volume charge, the Helmholtz layer, and the electrolyte respectively; and r_{SC}, r_H, and $\varkappa^{-1}$ are the Debye length (characterising the extent of the layer occupied by the volume charge), the extent of the Helmholtz layer, and the thickness of the Gouy layer respectively. The analytical[37] and graphical[38] solution of Eqns.(5) and (6) makes it possible to calculate quantitatively a large number of parameters characterising the distribution of the potential jump. It should be noted that the calculated value $r_{SC} = (\varepsilon_{SC}kT/4\pi e^2 n_0)^{1/2}$ depends on the concentration of free charges (n_0) in the oxide. If $n_0 = 1 \times 10^{13}$ cm^{-3}, and the concentration of ions in a 0.01 M solution of the electrolyte

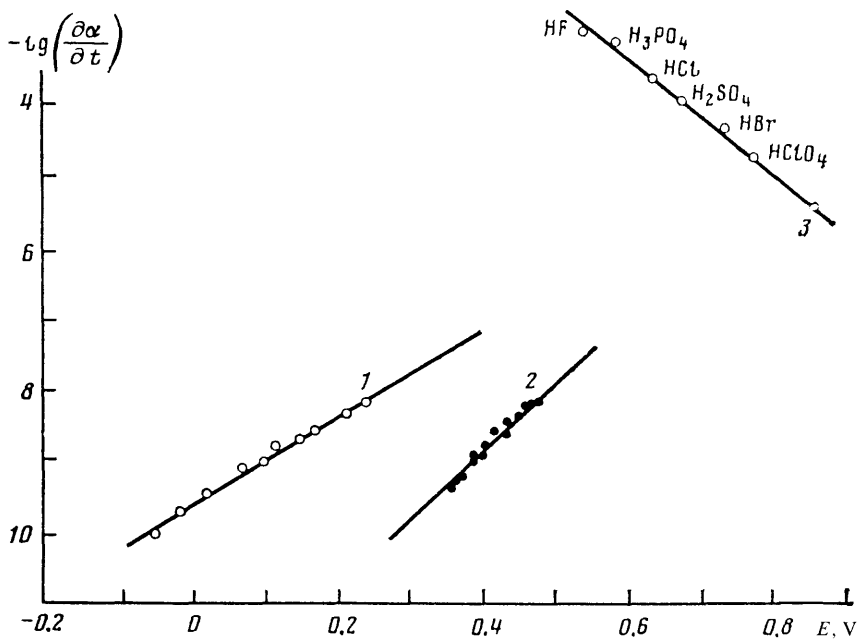


Figure 3. Dependence of the rate of dissolution on the potential for the following oxides: *1*) UO_2 (0.2 M Na_2CO_3 + 0.2 M $NaHCO_3$, 25 °C; $\partial E/\partial \lg \partial\alpha/\partial t$ = 150 mV); 2) UO_2 (1 M $HClO_4$, 25 °C; $\partial E/\partial \lg \partial\alpha/\partial t$ = 120 mV);[30] 3) Fe_2O_3 (1 M acid solutions, 50 °C; $\partial E/\partial \lg \partial\alpha/\partial t$ = 120 mV.[153]

is 10^{19} cm^{-3}, then the extent of the region occupied by the space charge ($r_{sc} \cong 10^{-4}$ cm) is 100 times the thickness of the diffuse layer. With increase in the concentration of free carriers (for example in the reduction of oxides showing *n*-conductivity), the quantity $r_{sc} \to 0$ as $n_0 \to \infty$. In this case all the space charge is "concentrated" on the electrode surface.

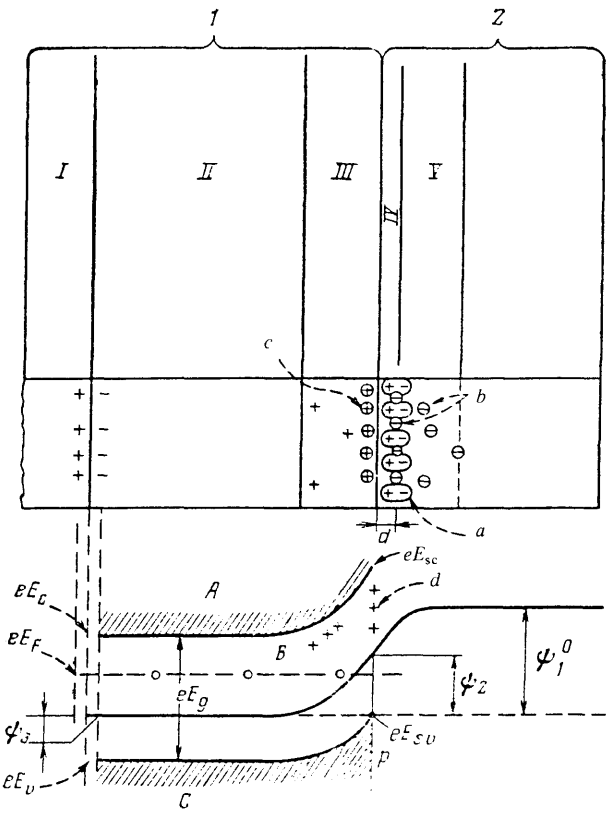


Figure 4. Structure of the electrical double layer at the oxide/electrolyte interface: *1*) solid phases: *I*) metal, *II*) oxide, *III*) region of space charge in the oxide; *2*) electrolyte: *IV*) Helmholtz layer, *V*) Gouy layer. Species creating the electrical double layer: *a*) oriented dipoles of water; *b*) excess ions of the solutions; *c*) adsorbed ions on the oxide, creating surface states; *d*) ionic states. Energy characteristics of the semiconductor (oxide): *A*) conductivity zone, *B*) non-compensated ions of the donors, *C*) valence zone; ψ_1, ψ_2, ψ_3 are the galvanic potentials of the solution, the surface states of the oxide phase, and the metal respectively.[73]

The rate of the dissolution of oxides is controlled chiefly by the magnitude of the potential in the Helmholtz layer. The magnitude of the potential in this case cannot be found experimentally. The values of the other components can be determined. For example, the magnitude of the potential E_{sc} is calculated from the dependence of the photopotential, the differential capacity, and the surface conductivity on the polarisation potential of an oxide electrode.[39-41] Usually, the value of the potential of the planar zones (E_{fb}), when $E_{sc} = 0$ and $E_{el} = 0$, was found. The values of E_{fb} are given in Table 1.

Table 1. Width of the band gap of metal oxides (eE_g) and the potentials of the planar zones of the electrodes [E_{fb}, V (normal electrode)] for different pH values.

Oxide	eE_g, eV	pH 2.0	pH 4.0	pH 6.0	pH 8.0	pH 10.0	pH 12.0	pH 14.0	Refs.
TiO_2	3.0	−0.14	−0.26	−0.38	−0.49	−0.61	−0.73	—	[42]
NiO*	from 1.72–1.90 to » 3.7	+0.97	+0.89	—	—	—	—	—	[43]
WO_3	2.4±0.1	+0.64	+0.51	+0.39	+0.27	+0.15	—	—	[44]
ZnO	3.2	+0.09	−0.02	−0.14	−0.24	−0.34	—	—	[45]
SnO_2	3.5±0.1	+0.36	+0.17	−0.12	−0.32	—	—	—	[46]
SnO_2**	3.5±0.1	—	+0.09	−0.10	−0.28	−0.48	—	—	[46]
Fe_2O_3	2.2	—	—	+0.14	−0.11	−0.23	−0.34	−0.45	[47]

*p-Type conductivity; n-type conductivity in the other cases.

**Studied in an acetate buffer containing $Fe(EDTA)^{2-}/Fe.(EDTA)^{-}$.

In the study of the kinetics of the dissolution of oxides, it has been assumed that the rate of the process is limited by the potential jump in the Helmholtz layer.[29,48] The factors influencing its magnitude can therefore be considered.

a) Factors influencing the magnitude of the potential in the Helmholtz layer. At $E_{sc} = 0$ (that is in the absence of a potential jump in the region of the space charge), the magnitude of the total E is determined by the potential jump in the Helmholtz layer. The study of the influence of various factors[32] on the potential of the planar zones is now not only a stimulus to study but also one of the methods for studying this layer. On oxides (ZnO, TiO_2, SnO_2, Fe_2O_3), the magnitude of E_H is a linear function of pH

$$E_H = E^0 - \left(\frac{2.3\,kT}{e}\right)(\mathrm{pH})$$

since the potential E_H is related to the concentration of adsorbed protons H^+ (the potential-determining ion). If it is assumed that the capacity C_H per unit surface area of the oxide electrode is independent of E_H, it follows that

$$e[H_s^+] = C_H E_H \qquad (7)$$

Here, the pH dependence is due to the reactions: $H_3O^+(aq) \to H^+(solid) + H_2O(aq)$

$$MO_{x_1} + (x_1 - x_2)e + (x_1 - x_2)H^+ \to MO_{x_2} + (x_1 - x_2)H_2O$$
$$\Delta G^0 = \Delta G^0(MO_{x_2}) - \Delta G^0(MO_{x_1}) + \Delta G^0(H_2O)$$
$$\frac{[H^+(solid)]}{[H_3O^+(aq)]} = \exp\left(-\frac{\Delta G^0}{kT}\right) = A\exp\left(-\frac{eE_H}{kT}\right) \qquad (8)$$

Comparison of Eqns.(7) and (8) shows that $eE_H = B - 2.3\,kT$ (pH). If adsorption of other ions of the electrolyte takes place, it leads to a change in the magnitude of E_H.

This potential jump is practically independent of the polarising potential, and its magnitude is not influenced by ions which have not been adsorbed on the electrode. The reason is that the extent of the Helmholtz layer is smaller than the thickness of the layer of the space charge. When charge is transferred from the volume to the surface of the semiconductor, only a small fraction of the consequent change in

the potential difference corresponds to E_H. The decrease in potential takes place chiefly in the region of the space charge, and not in the Helmholtz layer. The potential jump in the Helmholtz layer at the oxide/electrolyte boundary depends on the surface properties of the semiconductor, the ionic strength of the electrolyte, the pH of the solution, and the specific adsorption. The change in potential in the Helmholtz layer is due to the establishment of equlibrium between the solution and the oxide electrode.[49] When the oxides come into contact with the electrolyte solutions, a surface charge is produced as a result of the dissociation of acidic and basic groups; this process can be represented by the equations

$$HOMO^- + H^+ \overset{K_+}{\leftarrow} MO(solid) + H_2O \overset{K_-}{\rightarrow} MOH^+ + OH^-$$

where K_+ and K_- are the dissociation constants of the acidic and basic groups respectively.

Table 2. Electrocapillary zero at 25 °C and the isoelectric point of metal oxides.

Oxide	Coordination	Structure	$pH_{e.z.}$	$pH_{i.p.}$ (Ref.51)	
				hydrate	anhydrous
Cu_2O	2—4	oct.	>11.5	—	9.5±0.4
MgO	6—6	cub.	12.4	—	12.4±0.3
CdO	6—6	cub.	10.4	>10.5	10.4±0.2
NiO	6—6	cub.	9.85*	—	10.3±0.4
CuO	6—6	cub.	9.5	—	9.5±0.4
ZnO	4—4	hex.	9—10	10.3	9.3
α-Al_2O_3	6—4	hex.	6.5—9.5	9.2	6.7
α-Fe_2O_3	6—4	rhomb.	8.5	8.0±0.2	6.5
α-Cr_2O_3	6—4	rhomb.	7.0	7.29	6.49
UO_2	8—4	cub.	3.5—6.5	—	5.8±0.2
TiO_2	6—3	tetr.	4.7	6.0±0.3	3.5±0.2
SnO_2	6—3	tetr.	5.5	5.5	4.7
β-MnO_2	6—3	tetr.	7.0	—	4.0—4.5
WO_3	6—2	rhomb.	0.5	<0.3	—
Co_3O_4	—	cub.	10.35*	—	—
Fe_3O_4	—	cub.	6.4**	—	6.5±0.2

Note: oct. = octahedral, cub. = cubic, hex. = hexagonal, rhomb. = rhombohedral, tetr. = tetragonal symmetry. The pH values at the electrocapillary zero at 40, 60, and 80 °C for NiO are 9.58, 9.25, and 9.06 respectively, and those for Co_3O_4 are 10.04, 9.82, and 9.62.[52]

*Data from Ref.52; **data from Ref.2; for the other oxides—data from Ref.4.

For oxides, the potential-determining ions are usually hydrogen cations or hydroxide anions.[50] In the case of oxides, a change in pH has a significant influence on the sign of the surface charge. There exists a state of the solution (pH value) corresponding to the electrocapillary maxima, when the oxide surface has equal numbers of positive and negative groups. This point (the electrocapillary zero) is the most important parameter of the interface. The electrocapillary zero (e.z.) of an oxide (Table 2) is related to the change in the surface charge. Thus the surface charge (σ_0) is usually described using the specific adsorption of the potential-determining ions (H^+ or OH^-): $\sigma_0 = eF(\Gamma_{H^+} - \Gamma_{OH^-})$, where F is the Faraday number, and Γ_{H^+} and Γ_{OH^-} the quantities of adsorbed protons and hydroxide ions respectively. This charge leads to the production of a potential which changes with increase in the distance from the surface. The state of the solution corresponding to zero potential is called the isoelectric point (i.p.). In the absence of specific adsorption, that is in a solution of an indifferent electrolyte, the electrocapillary zero and the isoelectric point coincide (zero zeta-potential).

The value of the $pH_{i.p.}$ for oxides changes systematically with change in the properties of the cation. A study of 18 oxides[51] showed that the change is described by the equation

$$pH_{i.p.} = 18.6 - 11.5\ (z/r)$$

where z is the charge of the cation, and r the distance between the adsorbed proton and the cation (equal to the diameter of the oxygen ion plus the radius of the cation). It has been proved experimentally[53,54] that the position of the electrocapillary zero is related to the average electrostatic field in the oxide lattice.

It is of interest to try to find a correlation between the potential jump in the Helmholtz layer (E_H) and the magnitude of the surface charge. According to the ion–dipole model,[55,56] E is separated into the internal potential E_H and the psi-potential (ψ_1):

$$d\psi_1 = -59.2\, d\ (pH).$$

In the case of an oxide, the surface potential is given by more complicated equations.[57,58] Determination of the values of the electrocapillary zero and the isoelectric point on oxides has shown that their values depend on the structure of the surface and on the orientation of the atoms in the crystal (deviation from an ideal crystal usually displaces the isoelectric point towards the more acidic range), on the degree of surface hydration (with increase in the degree of hydration, the isoelectric point corresponds to a higher pH value[59]), and on the magnitude of the charge of the cation in the oxide,[59] the nature of the semiconducting properties of the oxide,[59] the presence of impurities, etc. The pH corresponding to the electrocapillary zero is also influenced by various factors,[59,60] some of which are indicated in Table 2.

A correlation exists between the position of the electrocapillary zero and the rate of dissolution of oxides. The lower the pH corresponding to the electrocapillary zero, the more difficult the dissolution of the oxide. Thus under identical conditions, ZnO and Cu_2O dissolve in acids much more rapidly than TiO_2, α-Cr_2O_3, and α-Fe_2O_3,[59] and the values of the pH at the electrocapillary zero are correspondingly much higher for zinc and copper(I) oxides. With increase in temperature, the electrocapillary zero for a number of specimens (oxides) studied is displaced into the acidic range.[52] The isoelectric point is displaced to higher pH values for hydrated specimens, compared with non-hydrated specimens, so that the former usually dissolves more readily.[51,59] At pH values above the electrocapillary zero, the oxide surface is negatively charged as a result of the strong adsorption of OH^- groups. The magnitude of the surface charge (q_-) decreases with decrease in pH. The magnitude of the positive charge (for example for haematite) depends chiefly on the activity a_{H^+}, and depends little on the anionic composition of the electrolyte.[59]

The surface charge is determined chiefly by the desorption of H^+ on the neutral surface. In some electrolytes (of the KCl type), q_+ depends not only on a_{H^+} but also on a_{Cl^-}. Under these conditions, the surface OH^- groups are displaced by Cl^- ions:

$$\left[\begin{array}{l}\diagdown\\ \text{—FeOH}(OH)_2\\ \diagup\end{array}\right]^- \underset{OH^-}{\overset{2H^+,Cl^-}{\rightleftharpoons}} \left[\begin{array}{l}\diagdown\\ \text{—Fe}(H_2O)_2^{2+}Cl^-\\ \diagup\end{array}\right]^+ + OH^-$$

There are two approaches to the solution of the problem of the nature of the potential jump. Quasi-equilibrium[34,35] and non-equilibrium (compromise)[49,61,62] potential jumps are distinguished. The reactions taking place at the oxide/electrolyte interface determine the magnitude of the potential jump and the rate of dissolution of the oxide in the acid.

b) Principal types of quasi-equilibrium reaction determining the magnitude of the potential jump in the Helmholtz layer. According to the theories of electrochemical kinetics, the magnitude of the potential jump at a phase boundary may be determined both by the exchange of hydrogen cations and metal ions between the oxide phase and the electrolyte solution and also by reactions of other types.[29,34,49,62,63] It is suggested that the potential-determining reactions in a multi-stage process of oxide dissolution are close to equilibrium (quasi-equilibrium), since the current due to the exchange of the potential-determining ions of the oxide phase[64] is greater than the current due to the dissolution of the oxides.[2]

Analysis of experimental data on the potential (E) for FeO_x and MnO_x electrodes shows that E is a complex function of pH, x, and $\ln a_{M^{2+}}$. In strongly acidic media, the magnitude of E is determined by the reaction

$$M^{3+}+e=M^{2+} \qquad (9)$$

and obeys the Nernst equation

$$E = E^0 + \frac{RT}{F} \ln \frac{[M^{3+}]}{[M^{2+}]}$$

In media close to neutral, the dependence of the potential on various factors (in the absence of M^{2+} ions) is determined by the parameters[49]

$$\partial E/\partial \ln[M^{2+}] \sim 0;\ \partial E/\partial(\mathrm{pH}) = 0.059;\ E^0 = f(x) \qquad (10)$$

and the value of E is determined by a reaction of the form:

$$MO_{x_1} + 2(x_1 - x_2)H^+ + 2(x_1 - x_2)e \rightarrow MO_{x_2} + (x_1 - x_2)H_2O$$

The potential may be linearly dependent on the stoichiometry of the oxide: $E^0 = a + bx$, or be determined by the expression:

$$E = E^0 + \frac{RT}{F} \ln \frac{[M^{z+}]}{[M^{(z-1)+}]} \qquad (11)$$

In the presence of M^{2+} ions (at the same pH values):[49]

$$\partial E/\partial \lg[M^{+2}] = -\frac{1}{x-1}0.029;\ \partial E/\partial(\mathrm{pH}) = -\frac{x}{x-1}0.059;\ E^0 = f(x) \qquad (12)$$

The change from Eqn.(10) to Eqns.(11) and (12) is determined by the magnitude of the pH and the ratio $[M^{3+}]/[M^{2+}]$.

To explain the dependence of the magnitude of the potential of the manganese oxide electrode on various factors, it has been suggested that use be made of reaction (9), which in weakly acidic media is complicated by the disproportionation of Mn^{3+}:

$$Mn^{3+} + \frac{x}{2(x-1)}H_2O \rightarrow \frac{2x-3}{2(x-1)}Mn^{2+} + \frac{1}{2(x-1)}MnO_x + \frac{x}{x-1}H^+ \qquad (13)$$

In this case the magnitude of the potential (11) is determined by the overall reaction

$$MnO_x + 2(x-1)e + 2xH^+ \rightarrow Mn^{2+} + xH_2O \qquad (14)$$

and obeys the equation:[95]

$$E = -1.196 + 0.687\frac{x^2 - 0.155x}{x-1} - \frac{0.059x}{x-1}\mathrm{pH} - \frac{0.029}{x-1}\lg[Mn^{2+}] \qquad (15)$$

Eqn.(15) corresponds to the theoretical relationship (14), which can be calculated using the expression:

$$E = -\frac{\Delta G^0}{2(x-1)F} = -\frac{x\Delta G^0(H_2O) + \Delta G^0(Mn^{2+}) - \Delta G^0(MnO_x)}{2(x-1)F} \qquad (16)$$

The relationship between the free energies of formation of the oxides of 3d elements $[\Delta G^0(MnO_x)]$ and x is given by the equation

$$\frac{\Delta G^0_x}{x} = \frac{\Delta G^0_i}{i} - \frac{\Delta G^0_i/i - \Delta G^0_j/j}{i-j}(i-x) \qquad (17)$$

where ΔG^0_i and ΔG^0_j are the free energies of formation of the oxides MO_i and MO_j from the elements.[65,66]

Substituting Eqn.(17) in Eqn.(16) gives†

$$E = E^0_{M/M^{2+}} + \frac{\Delta G^0_i/i - \Delta G^0_j/j}{2(i-j)F}\cdot\frac{x^2 - [\Delta G^0_i(i-j)/(\Delta G^0_i/i - \Delta G^0_j/j) + 1]x}{x-1} - \frac{xRT\cdot 2.303}{F(x-1)}(\mathrm{pH}) - \frac{RT\cdot 2.303}{2(x-1)F}\lg[M^{2+}] \qquad (18)$$

which corresponds to the empirical equation (15) found experimentally. It is also possible to verify the dependence of $\Delta G^0(MnO_x)$ on x:

$$\Delta G^0(MnO_x)/x,\ \mathrm{kJ\ mole^{-1}\ (g\text{-}atom\ O)^{-1}} = -496.733 + 132.773\,x \qquad (19)$$

The published[67] and calculated values of $\Delta G^0(MnO_x)/x$ are compared below:

x	1.00	1.33	1.50	2.00	2.50	3.00
Calculated from Eqn. (19)	363.96	320.15	297.57	231.19	164.80	98.41
Published data (Ref.67)	363.86	321.16	293.72	233.68	—	98.38

The data given confirm the results of the determination of the magnitude of the potential at the manganese oxide/electrolyte interface.

Other reactions may determine the magnitude of the potential in the Helmholtz layer, when E depends on the stoichiometric composition of the oxide phase:

$$MO_{x_1} + 2(x_1 - x_2)H^+ + 2(x_1 - x_2)e \rightarrow MO_{x_2} + (x_1 - x_2)H_2O$$
$$E = E^0_{O_x} + a + b(x_1 + x_2) + RT/F\ln[H^+]$$
$$x_2MO_{x_1} + 2(x_1 - x_2)e + (x_1 - x_2)M^{2+} \rightarrow x_2MO_{x_2}$$
$$E = E^0_{M/M^{2+}} + bx_1x_2 + \frac{RT}{F}\ln[M^{2+}]$$

$$MO_x(\mathrm{solid}) + H^+(\mathrm{aq}) + e \rightarrow MO_xH(\mathrm{solid});\ E = E^0 + RT/F\ln[H^+]$$

where $a = [\Delta G_j^0/j)i - (\Delta G_i^0/i)j]/(i-j)F,\ b = (\Delta G_i^0/i - \Delta G_j^0/j)/2(i-j)F.$

The nature of the observed dependence of the potential of the oxide electrode on pH and $\lg a_{M^{2+}}$ is used to establish the form of the equilibrium, and Eqn.(18) is used to determine the phase composition of the oxide being studied, to refine the value of E, and to find the thermodynamic characteristics of the phase MO_x.[61,65,66]

c) The theory of stationary (compromise) potentials. A compromise potential jump is produced if the oxide is not in equilibrium with the electrolyte solution. A theory of stationary potentials has been developed.[68] According to this theory, at the stationary potential the sum of the cathodic currents is equal to the sum of the anodic currents

$$\sum k_+[\mathrm{Ox}]\exp\left(\frac{\beta_i z_i FE}{RT}\right) = \sum k_-[\mathrm{Red}]\exp\left(\frac{\beta_i z_i FE}{RT}\right) \qquad (20)$$

† Here,

$$\Delta G_i^0 = \Delta G^0(M^{2+}) + \Delta G^0(H_2O) - \Delta G^0(MO).$$

where k_+ and k_- are the rate constants of the anodic and cathodic reactions; β_j and β_i the transfer coefficients; and E the electrode potential. In the general form, this equation cannot be solved for E.

The kinetic equations of stationary potentials have been studied in detail.[69-71] The case of the production of a compromise potential jump at an oxide/electrolyte phase boundary has been examined.[72] According to the ideas developed, in the dissolution of an oxide the magnitude of E is determined by the parallel transfer of OH^-(solid) and M^{z+}(solid) to the electrolyte:

$$OH^-(solid) + H^+(aq) \rightarrow H_2O(aq);\ M^{z+}(solid) \rightarrow M^{z+}(aq)$$

The rates of these reactions depend on the potential. The driving force of the dissolution process is the magnitude of the potential drop in the Helmholtz layer. For $E_{sc}^0 = \text{const}$ and $E_{el} = 0$, the rates of the transfer of the M^{z+} ions (i_M) and OH^- ions (i_{OH}) to the solution can be written in the form:

$$i_M = {}_+k_M \exp(\beta_+ z_+ FE/RT) \quad (21)$$

$$i_{OH} = {}_-k_A a_{H^+} \exp(\beta_- z_- FE/RT) \quad (22)$$

The magnitude of the stationary potential is calculated by solving the simultaneous equations (21) and (22):

$$E = \frac{RT}{(\beta_+ z_+ - \beta_- z_-)F} \ln\left(\frac{k_-}{k_+} a_{H^+}\right) = E^0 - \frac{RT \cdot 2{,}303}{F(\beta_+ z_+ - \beta_- z_-)}(\text{pH}) \ . \quad (23)$$

The value of E obtained can be used to calculate the orders of the reaction with respect to H^+ and other ions.

Since there are two theories of the production of the potential jump (quasi-equilibrium and compromise), there are two approaches to the explanation of the reasons for the influence of E on the rate of the dissolution of oxides. A linear correlation is observed between E_{fb} and the value of E_{max} corresponding to the rate maximum.

2. Relationship Between the Semiconducting Properties of an Oxide and the Electrochemical Properties of the Electrolyte

A relationship exists between the semiconducting properties of an oxide and the electrochemical characteristics of the electrolyte solution–oxide system. The solution is characterised by the following electrochemical parameters: the standard oxidation (redox) potential for the redox couple (E^0), the average energy of the energy level of the molecule of the oxidising agent (unoccupied energy level) in the solution eE_{ox}, the average energy of the energy level of the molecule of the reducing agent (occupied energy level) in the solution eE_{red}, and the energy parameter of the solution eE_F, whose significance is analogous to that of the Fermi energy, since it is given by the relationship $eE_F = \frac{1}{2}(eE_{ox} + eE_{red}) = -E$.[36]

The properties of oxides as semiconductors are characterised by the following parameters: eE_v and eE_{vs} represent the energy of the top of the valence zone in the volume of the specimen and on the surface respectively, eE_F the Fermi energy, and eE_c and eE_{cs} the energies of the bottom of the conductivity zone in the volume and on the surface. The required relationship is established in explicit form by calculating and measuring the values of the potential of the planar zones (E_{fb}).

The comparison of the energy levels of the ions and the zone boundaries of an oxide on the same energy scale represents the most valuable contribution of the electrochemistry of semiconductors to the kinetics of the dissolution of oxides (see Fig.4). This comparison of the energy characteristics and electrochemical parameters is carried out as follows. The experimental relationship between the differential capacity of the oxide electrode (C_{SC}) and the polarisation potential of the oxide E (as $1/C_{SC}^2 \rightarrow 0$) is used to determine the value of E_{fb} from the Mott-Schottky equation:

$$\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon\varepsilon_0 e N_D}\left(eE_{sc} - \frac{kT}{e}\right) \quad (24)$$

According to Eqn.(24), when oxides are polarised, a linear relationship is usually observed between C_{SC}^{-2} and the polarisation potential of the oxide electrode. In this case, if $E_{el} \rightarrow 0$ (concentrated solution), the potential of the planar zones is measured:

$$E_{fb} \approx E_H + E^0 \quad (25)$$

In other words, the main potential jump corresponds to the Helmholtz layer. The linear relationships between C_{SC}^{-2} and E, obtained for oxides, indicate that the potential in the Helmholtz layer remains constant when the electrode is polarised; only the magnitude of the potential in the volume of the oxide phase is changed.[32] When E_{fb} has been determined, the electrochemical potential of the Fermi level of the oxide on the energy scale is found:

$$eE_{fb} = eE_F = -eE^0$$

For example, for ZnO, $eE_{fb} = -0.231$ eV (normal hydrogen electrode).[73] This result and Eqn.(25) give: $eE_F = -eE + eE^0 = +0.231 + (-4.5) = -4.269$ eV, where $eE^0 = 4.5$ eV[32] (see Fig.5). The values of eE_F and n and the known concentration N_c can then be used to determine the position of the bottom of the conductivity zone eE_c:

$$eE_F = eE_c - 2{,}3\ kT \lg(N_c/n) \ .$$

The width of the forbidden zone $eE_g = eE_c - eE_v$ can be used to find the positions of the zone boundaries.

The energy diagrams of the boundary of separation between the phases, constructed in this way, can be used to provide qualitative and semi-quantitative explanations for all the regular features of the dissolution of metal oxides in different media.

For example, the energy level diagram given in Fig.6 can be used to try to find which oxides can reduce hexacyanoferrate(III) ions by conductivity electrons, and which semiconductors by the injection of holes, that is by giving up electrons from the valence zone (see Fig.6, GaP and GaAs). These diagrams can be used only as the starting point for an analysis of the possible reactions between oxides and the ions of the liquid phase (solutions). To bring about the injection of electrons into an oxide, the energy of the levels eE_{red} should be equal to or greater than the energy of the unoccupied levels of the oxide, and for the capture of an electron by the ions, the energy of the level eE_{ox} should take values equal to or lower than the energy of the occupied levels. It has been found empirically[74] that injection of electrons is observed when the energy of the bottom of the conductivity zone of a semiconductor is higher than the energy $eE_{redox}^0 = -eE^0$ by not more than 0.8 eV. Thus the ions Cr^{2+}, Eu^{2+}, V^{2+}, and Co^{2+} inject electrons into ZnO ($eE^0 \gg 0.1$ eV).[75]

Surface reactions (such as dissolution) involving the oxides, together with reactions involving the ions which complicate the picture (hydrolysis, complex formation, dimerisation, the production of unstable states), make the situation much more complex.

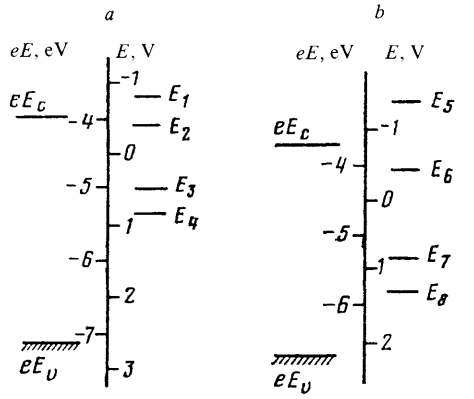


Figure 5. Positions of the energy zones of the oxide (*a*—ZnO, *b*—TiO_2) and the Fermi levels (potentials E_1–E_8) for various electrode reactions taking place at an oxide electrode in aqueous solution at pH 7: *1*) ZnO + $2H^+(aq)$ + $2e \rightarrow Zn + H_2O$ (E_1); *2*) $2H^+(aq) + 2e \rightleftharpoons H_2$ (E_2); *3*) ZnO + $2Cl^-(aq) + 2p \rightarrow ZnCl_2(aq) + \frac{1}{2}O_2$ (E_3); *4*) $H_2O + 2p \rightleftharpoons 2H^+(aq) + \frac{1}{2}O_2$ (E_4); *5*) $TiO_2 + 4H^+(aq) + 4e \rightarrow Ti + 2H_2O$ (E_5); *6*) $2H^+(aq) + 2e \rightleftharpoons H_2$ (E_6); *7*) $H_2O + 2p \rightleftharpoons 2H^+(aq) + \frac{1}{2}O_2$ (E_7); *8*) $TiO_2 + 4Cl^-(aq) + 4p \rightarrow TiCl_4(aq) + O_2$ (E_8).[85]

IV. FORMAL ELECTROCHEMICAL THEORIES OF THE DISSOLUTION OF METAL OXIDES

There are different versions of the theory of the influence of oxidising agents and reducing agents in an electrolyte on an oxide phase during its dissolution. The present-day physical theories of the reduction and oxidation of oxides as semiconductors, and classical electrochemical theories, explaining the mechanism of the influence of the potential on the dissolution of oxide materials, can be distinguished.

The dissolution of oxides is possible if the concentration of the ions in the electrolyte is lower than the saturation concentration. For a given deviation of the concentration from the limiting value, the rate of dissolution is related to the transfer reaction:

$$M^{z+}(solid) \rightarrow M^{z+}(aq);\ A^{z-}(solid) \rightarrow A^{z-}(aq)$$

For the dissolution of crystals in the absence of an external current, the densities of the transfer currents i_M and i_A are equal in magnitude, have different signs, and are conjugated. Volmer's equation[49] is used to describe the regular electrochemical features of the transfer of ions. The dependence of the rates of the transfer of the ions M^{z+} and A^{z-} to the solution on the potentials can be expressed by equations analogous to Eqns.(16) and (17):

$$i_M = {}_+k_M[M]\exp\left(\frac{\beta_+ z_+ F}{RT}E\right) - {}_-k_M a_{M^{z+}}\cdot\exp\left[-\frac{(1-\beta_+)z_+F}{RT}E\right] \quad (26)$$

$$i_A = {}_+k_A a_{A^{z-}}\exp\left(\frac{\beta_- z_- F}{RT}E\right) - {}_-k[A]\cdot\exp\left[-\frac{(1-\beta_-)z_-F}{RT}E\right] \quad (27)$$

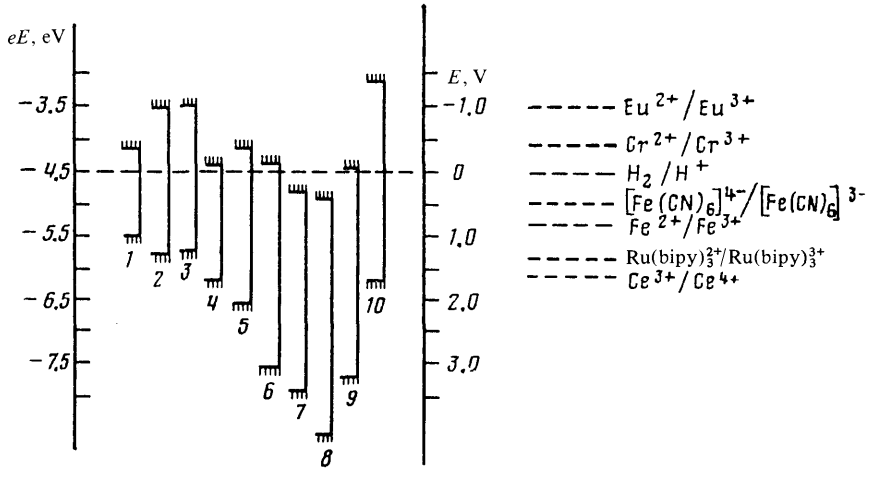


Figure 6. Relative positions of the energy levels of semiconductors and the Fermi levels for various redox reactions taking place at an electrode in aqueous solution: *1*) GaAs, pH 14; *2*) GaAsP, pH 14; *3*) GaP, pH 1; *4*) CdSe, pH 6; *5*) CdS, pH 6; *6*) ZnO, pH 2; *7*) SnO_2, pH 14; *8*) SnO_2, pH 1; *9*) TiO_2, pH 1; *10*) SiC, pH 1.[32]

1. Theory of the Conjugated Transfer of the Cations and Anions of an Oxide to an Electrolyte Solution

a) Jaenicke's theory of the dissolution of ionic crystals.[62,63] The transfer of cations is expressed by the anodic current (i_M), and the transfer of anions by the cathodic (i_A) current. The dissolution is associated with diffusion (through the electrical double layer of thickness δ) according to the equation:

$$i_d = i_M = -i_A = zFDc_M/\delta = zFDc_A/\delta$$

Jaenicke and Haase,[63] by combining Eqns.(26) and (27), and also taking account of the electrical neutrality condition ($a_{M^{z+}} = a_{A^{z-}}$), derived equations of the form:

$$i_d = \frac{\exp\left(\frac{zF\eta}{RT}\right) - \exp(-zF\eta/RT)}{\exp[(1-\beta_+)z_+F\eta/RT]/i_{e,M} - \exp[(-\beta_-z_-F\eta)/RT]/i_{e,A}} \quad (28)$$

where η is the overvoltage and $i_{e,M}$ and $i_{e,A}$ the exchange currents of the metal ions and the anions respectively;

$$c/c_{sat} = \exp\left(-\frac{zF\eta}{RT}\right)\left\{1 - \frac{i_{e,M}}{i_{e,A}}\exp\left[\frac{(1-\beta_-)+\beta_+}{RT}zF\eta\right]\right\} \Big/ \left\{1 - \frac{i_{e,M}}{i_{e,A}}\exp \times \right.$$
$$\left. \times\left[-\frac{1-\beta_+ + \beta_-}{RT}zF\eta\right]\right\} \quad (29)$$

It follows from Eqn.(29) that as $c/c_{sat} \to 0$, the maximum overvoltage ($\eta = \eta_{max}$) is observed

$$\eta_{max} = \eta = \frac{RT}{(1-\beta_- + \beta_+)zF}\ln\frac{i_{e,A}}{i_{e,M}}$$

which corresponds to the maximum rate of dissolution:

$$i_{d,max} = i_{e,A}^{\beta_+/(1-\beta_-+\beta_+)} \cdot i_{e,M}^{\beta_+/(1-\beta_-+\beta_+)}$$

For $\beta_+ = \beta_- = 0.5$:

$$i_{d,max} = (i_{e,A} \cdot i_{e,M})^{1/2} \quad (30)$$

Analysis of Eqn.(30) shows that the rate of dissolution depends on the magnitude of the exchange currents ($i_{e,A}$ and $i_{e,M}$). At low values of the overvoltage ($\eta \ll RT/zF$):

$$(\partial\eta/\partial i_d)_{\eta=0} = \frac{RT}{2zF}\left(\frac{1}{i_{e,M}} - \frac{1}{i_{e,A}}\right) \quad (31)$$

The applicability of relationships (30) and (31) has not yet been confirmed experimentally.

b) Engell's theory of the dissolution of oxide phases.[29] In the derivation of the $E(i)$ relationship, Engell made the following assumptions: 1) the processes involved in the transfer of the ions [M^{z+}(solid) → M^{z+}(aq); A^{z-}(solid) → A^{z-}(aq)] are independent; 2) the total value of the chemical potential for the anions (μ_A) and cations (μ_M) is constant, that is $\mu_M + \mu_A = \mu_\pm$; 3) the dissolution is a non-equilibrium process, since the reverse reaction is suppressed; 4) the fact that the composition is constant is explained by the fact that the fluxes of the ions (the cations i_M and the anions i_A) through the electrical double layer are the same ($|i_M| = |i_A|$); 5) the rate of dissolution depends on the potential in the Helmholtz layer, in accordance with the Volmer equation; and 6) the surface concentrations of the cations and anions are given by the Boltzmann equation:

$$[A] = \exp[(\mu_A - \mu_A^0)/RT];\ [M] = \exp[(\mu_M - \mu_M^0)/RT]$$

where μ_M^0 and μ_A^0 are the chemical potentials of the ions at the surface at an ion concentration $c = 1$.

Allowance for the above assumptions, Eqns.(26) and (27), and

$$k_+\exp(-\mu_A^0/RT) = k_A^0;\ k_-\exp\left(-\frac{\mu_M^0}{RT}\right) = k_M^0;$$

$$\mu_M = \frac{1}{2}\{\mu_\pm RT\ln(k_A^0/k_M^0) + (\beta_Az_A - \beta_Mz_M)FE\};$$

$$\mu_A = \frac{1}{2}\{\mu_\pm + RT\ln(k_M^0/k_A^0) + (\beta_Az_A - \beta_Mz_M)FE\}$$

gives for $z_A = -z_A$

$$i_M = i_A = (k_A^0k_M^0)^{1/2}\exp(\mu_\pm/2RT)\exp[\{\beta_M|z_M| - \beta_A|z_A|\}FE/2RT] \quad (32)$$

It follows from Eqn.(32) that the slope of the Tafel section is

$$\partial E/\partial\ln i = 2RT/F(\beta_M|z_M| - \beta_A|z_A|)$$

If $\beta_Az_A > \beta_Mz_M$, an increase in the rate is observed with decrease in the potential. The values of the slope have been given[29] for cases where the dissolution is limited by the transfer of the anions

$$\partial E/\partial\ln i = (z_M - \beta_A|z_A|)F/RT$$

or the cations

$$\partial E/\partial\ln i = [\beta_Mz_M - |z_M|]F/RT$$

Thus for FeO,[29] $\partial E/\partial\ln i = 0.080$ V. Since

$$z_{Fe^{2+}} = 2,\ z_{O^{2-}} = -2, \text{ it follows that } (\beta_{O^{2-}} - \beta_{Fe^{2+}}) = 0.32$$

Some aspects of Engell's theory have led to a number of comments:[2,48] 1) Engell regards oxides as purely ionic compounds, completely ignoring the influence of the important semiconducting properties of oxides (volume charge, electron and hole conductivity, energy of the levels); 2) according to Engell, the polarisation potential corresponds only to the region of the volume charge (the potential jump in the Helmholtz layer is not taken into account); and 3) some of the assumptions made by Engell exclude even slight deviation from stoichiometry.

c) Vermilyea's theory of the dissolution of oxide phases[72] makes it possible to explain the formal orders of the reaction with respect to hydrogen ions, the dependence of the rate of dissolution on the potential, and the influence of the anion composition of the electrolyte. According to Vermilyea,[72] the dissolution is an electrochemical process, and consists of two conjugated reactions, involving the transfer to the solution of the metal ions and oxygen ions.

Vermilyea established the dependence of the rate of dissolution on the potential by making use of the following assumptions: a) the dissolution process is irreversible; b) the concentration of ions on the surface is equal to $2n^0$:

$$[M] + [A] = 2n^0$$

where it follows from the last expression that deviations from stoichiometry are possible; and c) the rate of removal of the anions and cations are equal, that is $i_M = i_A$. From Eqns. (26) and (27) and assumptions (a)–(c), taking account of the fact that

$$_+k_M^0[M]\exp(\beta_+z_+FE/RT) = {}_+k_A[A]\exp(\beta_-z_-FE/RT)$$

it can be shown that the rate of dissolution is equal to

$$i_A = 2i_0[\exp(-\beta_-z_-F\eta/RT) + \exp(-\beta_+z_+F\eta/RT) \quad (33)$$

where the rate of free dissolution of the oxide (the magnitude of the potential is E_f) is:

$$i_0 = k_A^0\exp(\beta_-z_-FE_f/RT);\ \eta = E - E_f$$

If η is very small, it follows that

$$i_A = 2i_0[2 - (\beta_+z_+ + \beta_-z_-)\eta F/RT]^{-1} \quad (34)$$

The result obtained agrees with Engell's conclusion.[29] Eqn.(33) provides a fairly realistic explanation of the nature and existence of the maximum of the dependence of the rate of the dissolution of oxide phases on the potential.

In the case of cathodic polarisation, when the magnitude of the anodic current (i_A) can be neglected, Eqn.(33) becomes

$$i_A = kc^m_{H^+} \exp(\beta_- z_- F\eta/RT)$$

where $\eta \gg 0$. For $\beta_- = 0.5$ and $z_- = 1$, the calculation gives the value $\partial E/\partial \ln i = 120$ mV, which agrees with the experimental data.[76-78]

The above theories start from the assumption that the currents of the metal and oxygen ions are equal, that is that these transfer reactions are conjugated. Usually, the rate of removal of the ions is such that $i_M \gg i_A$ or $i_A \gg i_M$, so that the rate of dissolution is determined by the transfer of one particular ion. In this case the dissolution current is much smaller than the current of the exchange with respect to the metal ions and with respect to the anions.

2. Electron–Proton Theory of the Influence of the Potential

According to the electron–proton theory, the influence of the potential on the boundary of separation is revealed in the fact that the proton brings about mass transfer. Its first stage includes the electrochemical process of the transfer of protons through the oxide/solution interface and their adsorption on the surface of the oxide:

$$M^{z+}(solid) + O^{2-}(solid) + H^+(aq) + e \rightarrow OH^-(solid) + M^{(z-1)+}(solid)$$

where $M^{z+}(solid)$, $M^{(z-1)+}(solid)$, $O^{2-}(solid)$, and $OH^-(solid)$ are the species of the oxide phase. As a result of this reaction, the surface layer of the oxide is converted into a compound with variable (non-stoichiometric) composition. The concentration of protons present as OH groups, the electrical conductivity, and the stoichiometry of oxide are related to one another and depend on E. The second stage involves the "diffusion" of the atoms into the depth of the oxide phase with the simultaneous transfer of an electron from one metal ion to another, or dissociative diffusion. When the value of the potential is displaced into the cathodic range, the rate of the introduction of protons into the oxide increases. Their concentration in the oxide depends on the mobility of H^+ and on the magnitude of E.

The electron–proton theory is confirmed by a number of facts. Data obtained using hydrogen and oxygen isotopes indicate that hydrogen, and not oxygen, is transferred from the electrolyte solution into the oxide and in the opposite direction.[79,80] The fact that the cathodic and anodic charging curves show hysteresis, and also the slow changes in the current after the polarisation current is switched off, indicate that there is retarded diffusion of the protons.[34] The high rate of the electrochemical processes indicates that they involve fairly mobile species (the proton).

The participation of the protons in the electrochemical processes explains the differences in activity observed for hydrated and non-hydrated oxides. The introduction of protons into an oxide does not lead to a significant change in the crystal lattice parameters of the oxide.[34,81] It has been established that the rate of dissolution and the magnitude of the potential are directly proportional to the quantity of adsorbed protons [H^+(ads) ions[82]]:

$$i_d = (\partial\alpha/\partial t)_{sp} = K'[H^+(solid)] = K\theta_{H^+}$$

where θ_{H^+} is the degree of covering of the oxide surface by protons. It is known that the dependence of the degree of covering of a surface by adsorbed protons on the equilibrium concentration of the acid corresponds to the Freundlich equation[59,83]

$$\theta_{H^+} = Ba^n_{H^+}$$

where $n = 0.5$–0.6.

The above arguments have been used to derive# the dependence of the specific rate of dissolution of an oxide on the adsorption of H^+ ions on the oxide, the pH of the electrolyte, and E:

$$(\partial\alpha/\partial t)_{sp} = k \cdot a^m_{H^+} \exp[-(1-\beta_+)z_+FE/RT] \quad (35)$$

This expression makes it possible to explain all the regular kinetic features of the influence of H^+, E, and T on the specific rate of dissolution of oxide phases.

The order of the rate of dissolution of oxides with respect to hydrogen ions, $n_{H^+} = m$, should be 0.5. When E is displaced into the cathodic range, the rate of dissolution of the oxide should increase. The species taking part in the dissolution process is the proton.

For $\beta_+ = 0.5$ and $z_+ = 1$, the value of $\partial E/\partial \lg[(\partial\alpha/\partial t)_{sp}]$ should be 120 mV, which agrees with the experimental data.

V. THE SEMICONDUCTOR THEORY OF THE OXIDATION AND REDUCTION OF OXIDE PHASES

A different approach has been developed[35,36,84,86] for describing the regular kinetic features of the dissolution of oxides, which are semiconductors, in electrolytes containing added oxidising agents and reducing agents. According to this theory, when oxides are brought into contact with electrolyte solutions, transfer of electrons to the semiconductor from the ions of the solution, or in the opposite direction, this is due to the fact that the Fermi level (eE_F) in the oxide does not correspond to the Fermi level ($eE_{F,el}$) of the ions of the electrolyte.

When there is electrochemical polarisation of oxides in solutions of electrolytes having an oxidation potential E^0, an increase in their rate of dissolution in acidic media is possible. The thermodynamic conditions for the processes involved in the dissolution of oxide phases have been examined.[84] The thermodynamic data can be used to determine the standard potentials of the reactions involved in the cathodic and anodic decomposition of oxide materials. If $E < E^{decomp}$ or $eE_F > eE^{decomp}$, cathodic dissolution of the oxides, taking place with the participation of the electrons of the conductivity zone, is possible (see Fig.5). When $E > E^{decomp}_d$ or $eE < eE^{decomp}_d$, anodic dissolution of the oxides with the participation of the electrons of the conductivity zone is possible. For example, for the dissolution of zinc oxides with anodic polarisation of the electrode, these reactions can be represented in the form:

$$ZnO + p + H^+ \rightarrow Zn^{2+} + {}^1/_2H_2O_2$$

$$\Delta G^0_d = \Delta G^0(Zn^{2+}) + {}^1/_2\Delta G^0(H_2O_2) - \Delta G^0(ZnO) = -87.8 \text{ kJ mole}^{-1},$$

and the decomposition potential will be equal to:

$$E = -\Delta G^0_d/F = 0.91 \text{ V}.$$

The mechanism of the oxidation or reduction of oxides during dissolution with potentiostatic polarisation can also be explained with allowance for the semiconducting properties of the oxide phases. The transfer of electrons with polarisation, and the corresponding current, can be calculated

For a discussion of this topic see Refs.153, 166, and 209.

qualitatively using the diagram giving the distribution of the energy levels at the boundary of separation between the phases. The electrochemical reactions of oxide electrodes involve both electrons and holes. For an exchange reaction to take place on the surface of oxides, transfer must take place to levels situated close to the bottom of the conductivity zone or close to the top of the valence zone.[75] The positions of the characteristic energy levels in oxides (for example the bottom of the conductivity zone in a semiconductor) can be determined unambiguously, but in electrolyte solutions it is necessary to consider only the average values of the characteristic energies of the ions in the liquid (that is to take account of the fluctuation of the energy levels). These levels can be described by a Gaussian distribution function[32,88,89] (see Fig.7):

$$D(E) = W(E) = (4\pi kT\lambda_i)^{-1/2} \exp[-(eE - eE_{redox})^2/4kT\lambda_i]$$

where λ_i is the energy of the reorganisation of the environment which takes place as a result of the transfer of electrons from the electrode to the reagents in the solution as a result of the change in the charge of the particles. If it is necessary to determine, for example, the rate of transfer of an electron from the donor to the electrode, it can be expressed in terms of the rate of electron exchange between two isoenergetic levels in the electrode and in the solution, where the first of these levels is occupied, and the second is unoccupied. The rate of the redox reaction at the oxide surface is determined by the surface concentration of current carriers at the boundary of separation between the phases.[36] The expression for the exchange current of redox reactions at the boundary of separation should include the values of the standard redox potential E^0_{redox} and the concentrations of the reagents c_{red} and c_{ox}. It is possible to distinguish two cases (for *n*- and *p*-type semiconductors). The current of the electron transfer (i) from the valence zone of the semiconductor into the solution and on to the species being reduced, the acceptor (Ox), can be calculated. This reaction can be regarded as the transfer of a hole (p) from the acceptor into the valence zone:

$$Ox \rightarrow Ox^- + p$$

The rate of the process in this case will be directly proportional to the concentration of carriers in the valence zone and the density of acceptors (oxidising agent), which can capture an electron. Account must be taken of the fact that this exchange reaction can take place when the levels are situated close to the bottom of the conductivity zone or near the top of the valence zone. The transfer of an electron from the electrode to the acceptor is equivalent to the passage of an anodic current

$$i = c_{ox} \int_{-\infty}^{\infty} D(E)\, k(E)\, n(E)\, dE$$

where $D(E)$ is the probability of the distribution of the reagent particles with respect to energy, which can be described by a Gaussian distribution function; $n(E)$ the partial concentration of electrons (close to the surface of the semiconductor), whose energy is equal to eE; and $k(E)$ is the rate of the transfer of an electron with energy eE from the semiconductor to an ion in the solution having an energy eE'. Since the values of the functions $n(E)$ in the valence zone and $k(E)$ are practically constant for $eE \cong eE_S$, and the energy of the top of the valence zone close to the surface differs by an amount $-eE_{SC}$ from the energy of the top of the valence zone in the volume of the semiconductor (eE_V), it follows that the final expression for the current has the form:

$$i = kc_A \exp\{(eE^0 - eE_A)^2/4kT\lambda_i\} \qquad (36)$$

According to Eqn.(36), the rate of the process will be a maximum when the magnitude of the energy of the energy level of the acceptor eE_A is equal to the energy of the surface state. Eqn.(36) has been verified experimentally.[87] For ZnO, it was found that the value of the potential E^0 corresponding to the maximum of the exchange current is 0.8 V. Since $eE^0_{redox} = -eE^0$, it follows that $eE_{CS} = eE^0_{ox} = eE^0_{redox} + \lambda_i = -0.8 + \lambda_i$.

The current of the electron transfer from the species being oxidised, the donor (D_{red}), in the solution to an energy level of the surface states of the oxide can be found analogously. The corresponding reaction can be written in the form:

$$D = D^+ + e$$

For the calculation of the current it is possible to obtain a

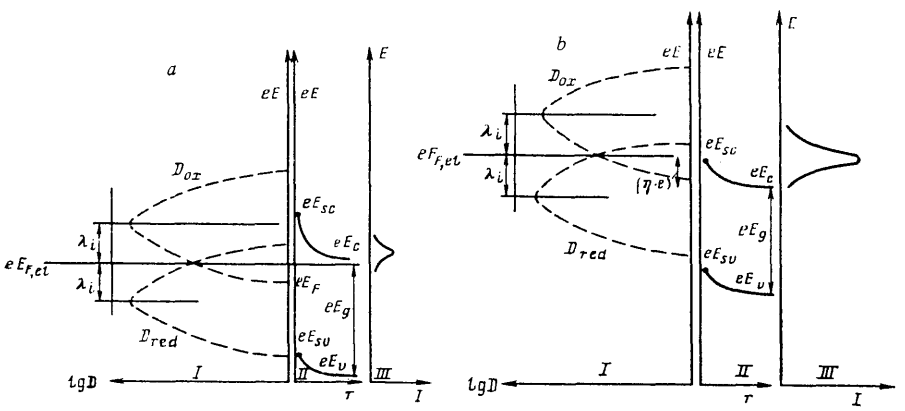


Figure 7. Positions of the energies at the semiconductor–solution interface for equilibrium (*a*) and for anodic polarisation of the semiconducting electrode (*b*): *I*) plot of the logarithm of the probability of the electrolyte redox species distribution against the magnitude of the energy, *II*) dependence of the position of the energy zones of the oxide on the distance from the interface, *III*) dependence of the current of the dissolution of the oxide phase on the magnitude of the applied voltage.[88]

relationship analogous to that proposed above:

$$i=kc_d\exp[(-eE-eE_d)^2/4kT\lambda_i] \quad (37)$$

Comparison of Eqns.(36) and (37) shows that the dependence of the current of the transfer of electrons on the potential passes through a maximum.[32] These regular features make it possible to explain the dependence of the rate of dissolution on the potential of the redox couples for oxides which are *p*- or *n*-type semiconductors.

Since the above theories are formal, it is of interest to examine the mechanism of the cathodic reduction or anodic oxidation of oxide phases and to discuss the question of why polarisation influences the rate of their dissolution.

VI. MECHANISM OF THE DISSOLUTION OF METAL OXIDES WITH CATHODIC AND ANODIC POLARISATION

The rates of these processes are limited by the magnitude of the potential of the redox reactions taking place on the surface of the oxide phase.[2] When the value of the stationary potential is displaced into the cathodic region, the rates of the dissolution of iron and manganese oxides increase.[2,90,91] The polarisation curves obtained for the polarisation of MnO_2 show two reduction waves, whose potentials depend on the concentration of metal ions and on pH. The peaks correspond to two processes:

$$MnO_2+H^++e\rightarrow MnOOH \quad (I)$$

$$MnOOH+H^++e\rightarrow Mn(OH)_2\rightarrow Mn^{2+} \quad (II)$$

The form of the polarisation curves ($E-i$) corresponds to the dependence of the rate of dissolution of the oxides Mn_2O_3, Fe_3O_4, and Fe_2O_3 on the potential.[90,91] There are two theories of the reduction of metal oxides. According to the first theory,[92–94] the reduction of an oxide phase is limited by the rate of removal of metal ions from it (Mn^{2+} for MnO_2 or Fe^{2+} for Fe_3O_4 and Fe_2O_3):

$$MO_x+2xH^++2(x-1)e\rightarrow M^{2+}+xH_2O$$

It is considered that MnO_2 (or Fe_3O_4) reacts as a reversible electrode, whose potential is determined by the concentration of metal ions M^{2+} and by the pH,[95,96] and $\partial E/\partial(pH) = 120$ mV/pH in the presence of both Mn^{2+} ions[95] and Fe^{2+} ions.[96] The quantity of electricity used up in this process[77] is twice that required for the reaction.[97] According to the theory being considered, the MnOOH formed is not the primary product, but is produced as a result of the reaction:[92,93,97–99]

$$MnO_2+Mn^{2+}+2H_2O\rightarrow\rightarrow 2MnOOH+2H^+$$

According to the second theory, the reduction of metal oxides is limited by the introduction of protons into the oxide phase. The reduction of the oxides takes place as a result of the transfer of protons through the electrolyte/oxide interface,[34,98–100] and is described by the equation:

$$MO_x(solid)+mH^+(aq)+me\rightarrow MO_{x-m}OH_m(solid)$$

There is no doubt that the last reaction takes place in alkaline media. The proton mechanism is confirmed by the ($E-i$, $i-t$) curves, which show the phenomena of concentration polarisation in the solid phase.[34] In the reduction of the oxides, the initial process is the adsorption of protons (to give OH groups); in the subsequent reduction, the hydrogen atoms diffuse into the oxide phase, leading to the reduction of deeper layers. The slow diffusion of hydrogen atoms brings about concentration polarisation in the solid phase.[34] X-Ray diffraction study of the products of the oxidation or disproportionation of magnetite has confirmed that under these conditions, a continuous series of solid solutions of Fe_3O_4 in γ-Fe_2O_3 is formed.[101] The yield of the cathodic process for the reaction for the most part never exceeds 100%; a solid solution of M_2O_3 in MO_2 or a solution of MOOH in MO_2 is formed.[102] The mechanism of the diffusion of protons has been examined quantitatively.[103,104] The presence of combined water in the oxides leads to an increase in the rate of diffusion of H^+.[34] The theory of the limiting stage of the diffusion of protons into the oxide does not explain the appearance in the electrolyte (in appreciable quantities) of Fe^{2+} and Mn^{2+} ions (at pH < 6) for the cathodic polarisation of Fe_2O_3 and MnO_2 respectively.

The theories can be combined by assuming that the chemical stage is complicated by a subsequent process. Using the last of the above equations for the reactions and taking account of the possible disproportionation of manganese(III) oxide gives:[76,105,106]

$$\begin{array}{l} 2(MnO_2+H^++e\rightarrow MnOOH) \\ 2\,MnOOH+2\,H^+\rightarrow MnO_2+Mn^{2+}+2\,H_2O \\ \hline MnO_2+4\,H^++2e\rightarrow Mn^{2+}+2\,H_2O \end{array}$$

Studies of the kinetics of the dissolution of the oxides NiO,[107] Cu_2O, CuO,[108,109] and UO_2[30] have shown that the rate of the process increases on anodic polarisation and when oxidising agents are introduced into the electrolyte solution.[30,109,110] The question of the stability of oxides on anodic polarisation is important not only in the study of their dissolution but also in practice, for the transformation of light energy into chemical energy. The question of the stability of oxides in acidic media has been studied.[36,84] It has been established experimentally that when holes are generated by anodic polarisation, illumination, or the addition of oxidising agents, there is an increase in the rate of dissolution, which (for example for ZnO) can be respresented in the form:

$$ZnO+2p\rightarrow Zn^{2+}+{}^1/_2O_2$$

In the dissolution of ZnO, oxygen is liberated, and Zn^{2+} ions are formed.[36,85,111–114] Similar results were obtained in the dissolution of copper oxides (Cu_2O, CuO),[85] which have hole conductivity and which decompose in acidic solutions with anodic polarisation to give Cu^{2+} and O_2. On the basis of potentiostatic measurements of the reduction and oxidation of a passivated nickel surface, a proton mechanism was proposed for the anodic polarisation of the oxides.[115–123]

1. Nature of the Active Centres and the Role of the Hydration of the Surface of Oxides in the Kinetics of Dissolution§

The dissolution of oxides begins on the active regions of their surface, as confirmed by etch figures. The introduction of the oxide TiO_2 into Fe_2O_3 (*n*-type semiconductor),[127] and also the addition of reducing agents to the acid solution, increases the rate of dissolution of iron(III) oxide, since there is an increase in the quantity of Fe^{2+} ions in the volume of the oxide phase.[2,128–130] The active centre for the dissolution in this case is Fe^{2+}. The rate of the dissolution of the oxides NiO and Cu_2O, which show *p*-type conductivity, increases when they are heated in an atmosphere with an increased oxygen pressure, and also when the value of the potential is displaced in the anodic direction. This is related to the fact that the active centres for the dissolution of NiO are Ni^{3+}.

§ For the bibliography on this topic, see Refs.53, 58, and 124–126.

The rate of the dissolution of oxides, and also their physical and chemical properties, are related to the degree of hydration of the surface.[4] A number of reviews[131–134] have been devoted to the study of the hydration and dehydration of oxide surfaces. Up to five types of isolated hydroxide group are usually distinguished on oxide surfaces. For example, the centre consisting of an OH group surrounded by four O^{2-} ions is the most basic, and a centre which has no neighbours (O^{2-} ions) is regarded as the most acidic. Acids react primarily with basic centres. The rate of the dissolution of ionic oxides is influenced considerably by change in the concentration of water in the acidic electrolyte. The rate of the dissolution of ZnO in alcoholic solutions of H_2SO_4 and HCl is slower by factors of 10^2–10^3 than that in aqueous solutions of the acids at the same concentrations.[135] A similar effect has been detected in the study of the kinetics of the dissolution of GeO_2 [10] and Al_2O_3 [136] in acids. The increase in the rate of dissolution of the oxides is directly proportional to the degree of hydration of the oxide phase.[10]

Another relationship was detected in studies of the influence of the concentration of acetone or ethylene glycol on the kinetics of the dissolution of Fe_3O_4 in HCl.[137,138] The rate of dissolution increases with increase in the concentrations of the acid, the iron(II) ions, and the non-aqueous solvents. The dependence of the time taken for 50% dissolution of Fe_3O_4 (0.5 g specimen) in 6 *N* HCl on the concentration (vol.%) of acetone and ethylene glycol is given below.

Acetone, vol. %	0	5	10	15	50	
$t_{0.5}$, min	47	41	23	15	1	
Ethylene glycol, vol.%	0	10	20	30	40	50
$t_{0.5}$, min	87	70	55	42	27	12

The rate of the dissolution is limited not by the reaction of magnetite with water molecules but by the process of proton transfer for the solution to the oxide phase. The increase in the rate of dissolution with increase in the concentration of non-aqueous solvents is related to the increase in the activity of the hydrogen ion (a_{H^+}) and the displacement of the potential (E_H) into the cathodic region.

2. Diffusion of Protons in the Oxide Phase During Its Dissolution

The study of the exchange equilibrium of ^2H and ^{18}O between a hydroxide and an electrolyte[34,139] has shown that the rate of the transfer of the hydrogen atoms is greater than that of the oxygen atoms. Linear scanning during the reduction of NiOOH gave the value of the proton diffusion coefficient ($D_{H^+} = 2 \times 10^{-9}$ cm^2 s^{-1}).[140] Higher values of the proton diffusion coefficient were observed during anodic polarisation, compared with the cathodic process. Other workers[141] have proposed a proton-diffusion process ($D_{H^+} = 2 \times 10^{-10}$ cm^2 s^{-1}) for the electrochemical formation of an NiOOH oxide film. Wyttenbach[142] gives the value $D_{H^+} = 4 \times 10^{-23}$ cm^2 s^{-1} (for the diffusion of H^+ at 25 °C) and $E_a = 96$ kJ mole^{-1}. The values of D_{H^+} for the other compounds are given below.

Compound	α-FeOOH	γ-AlOOH	NiOOH	δ-MnO_2
D_{H^+}, cm^{2}s^{-1}	$5.8 \cdot 10^{-17}$ [143, 144]	$5 \cdot 10^{-19}$ [145]	10^{-10}—10^{-11} [34]	10^{-18}—10^{-17} [139]

These values of the diffusion coefficients lie in a range between their values in electrolyte solutions and in the solid phase.

In electrochemical methods for determining the value of D_{H^+}, it is assumed that the rate of the redox processes is limited only by the diffusion of protons. The use of a potentiostatic method to study the formation of NiOOH during the anodic oxidation of Ni^{2+} ions[146,147] established, however, that the formation of $Ni(OH)_3$ is controlled by the change in the nature of the surface during the three-dimensional growth of the crystal. A noteworthy feature is the observed relationship between the diffusion of the protons and the semiconducting properties of the electrodes. In the opinion of Takehara and co-workers,[148] the surface concentration of the protonated regions and vacancies in oxides changes as a result of the reaction of charge transfer. The proton concentration gradient produced determines the rate of diffusion of H^+ between the surface and the volume of the oxide.

a) The specific features of the diffusion of protons.[12] Electrons move much more rapidly than protons, and lead to the appearance of a space charge, creating an electric field ($\partial E/\partial r$), which increases the velocity of the hydrogen ion flux (j_{H^+}).[149] The H^+ ion diffusion current will be:[150]

$$j_{H^+} = D_{H^+}\frac{\partial [H^+]}{\partial r} - \frac{D_{H^+}}{kT}[H^+]\frac{\partial E}{\partial r}. \qquad (38)$$

where $\partial[H^+]/\partial r$ is the proton concentration gradient in the oxide phase, j_{H^+} the velocity of the H^+ ion flux in the metal oxide, and D_{H^+} the proton diffusion coefficient in the oxide.

Eqn.(38) gave:

$$j_{H^+} = D_{H^+}\frac{\partial N_{H^+}}{\partial r}\{1 + N_{H^+}[N_D \exp(E_D - E_F)/kT + N_0 \exp(E_F - E_0)/kT]^{-1}\} \qquad (38a)$$

where N_D and N_{H^+} are the concentration densities of the donors and the protons respectively in the oxide.

Analysis of Eqn.(38a) shows that the effective proton diffusion coefficient (D_{eff}) in this case passed through a maximum as N_{H^+} increases with time and approaches N_D:

$$j_{H^+} = D_{H^+}\frac{\partial N_{H^+}}{\partial r}\left[1 + \frac{N_D}{N_{H^+} - N_D}\right] = \frac{\partial N_{H^+}}{\partial r} D_{eff} \qquad (39)$$

This result indicates that the rate of penetration of the protons into the oxide phase increases with time and passes through a maximum.

3. Dependence of the Specific Rate of Dissolution of Oxides on the Concentration of H^+ and Acids and on the Nature of the Electrolyte

The influence of the concentration of acids on the rate of dissolution of oxides has been the subject of a large number of studies.[2,4,12,13,17–20,151–166] The formal order of the reaction with respect to hydrogen ions (n_{H^+}) for the dissolution of oxide phases is ~0.5 (Table 3). When the dissolution is complicated by hydration, redox reactions, complex formation, and other factors, the formal order of the reaction with respect to acid takes different values. For the dissolution of iron(III) oxide in hydrochloric and hydrobromic acids, $n_{HA} \cong 2$,[18] and for the reaction of Fe_2O_3 with $HClO_4$, $n_{HA} = 0.9$.[18] The dependence of α on $t/t_{0.5}$ is invariant with respect to the acid concentration.[22] In most cases, the formal order of the reaction with respect to acids remains unchanged in the range of values of α 0.1–0.8.[22] This indicates that the morphology of the oxide phase/electrolyte interface remains unchanged for different values of α, and that the nature of the limiting stage of the process is independent of the acid concentration.

a) Interpretation of the order of the reaction according to Vermilyea's theory. According to Vermilyea's theory,[72] the mechanism of the dissolution of oxides is electrochemical, and

consists of two parallel reactions involving the transfer of H^+ and M^{z+} ions from the oxide to the solution. Substituting Eqn.(23) into Eqn.(21) shows that the rate of removal of the cations (M) will be:

$$i_M = a_{H^+}^{\beta_+ z_+/(\beta_+ z_+ - \beta_- z_-)} \cdot k_-^{\beta_+ z_+/(\beta_+ z_+ - \beta_- z_-)} / k_+^{\beta_- z_-/(\beta_+ z_+ - \beta_- z_-)} \qquad (40)$$

Table 3. Formal order of the reaction for the dissolution of metal oxides with respect to hydrogen ions (n_{H^+}) and acid (n_{HA}).

Oxide	Electrolyte	n_{H^+}	Oxide	HA	n_{HA}
MgO	HCl	0.47 [167]	Fe_2O_3	HCl	1.94 [18]
Fe_2O_3	HCl	0.5÷0.6 [48]	Fe_2O_3	H_2SO_4	0.56 [18]
Fe_2O_3	H_2SO_4	0.5÷0.6 [48]	Fe_2O_3	HF	1.06 [18]
Fe_2O_3	HNO_3	0.5÷0.6 [48]	Fe_2O_3	H_3PO_4	0.59 [18]
Fe_2O_3	$HClO_4$	0.5÷0.6 [48]	Fe_3O_4	HCl	2 [18]
Fe_3O_4	HCl	0.5 [31]	BeO	HCl, H_2SO_4, $H_2C_2O_4$	1 [154]
BeO	HCl	0.47÷0.53 [154]	MnO	H_2SO_4	2 [160]
BeO	H_2SO_4	0.68÷0.70 [154]	Fe_2O_3	HCl	2 [161]
V_2O_5	$HClO_4$	0.5 [155]	Fe_3O_4	HCl	3 [161]
Cr_2O_3	$HClO_4$	0.46 [156]	Fe_2O_3	HCl	2.4 [162]
Mn_2O_3	H_2SO_4	−0.5 [157]	NiO	H_2SO_4, HNO_3	1.0±0.1 [163]
α-Fe_2O_3	HNO_3	0.65 [158]	Ni_2O_3	H_2SO_4, HNO_3	1.0±0.1 [163]
Ni_2O_3	H_2SO_4	0.5±0.2 [159]	NiO, Ni_2O_3	HCl	0.6±0.1 [163]
MnO	H_2SO_4	0.5 [160]	CuO	H_2SO_4	1.0±0.1 [163]

Note. Numbers in square brackets denote references (Ed. of Translation).

Table 4. Dependence of the formal orders of the reaction with respect to H^+ ions (n_{H^+}) on the nature of the stage limiting the dissolution of the metal oxide*.

Limiting stage	n	ν	z_-	$z_+=1$	$z_+=2$	$z_+=3$	$z_+=4$
$OH^- + H^+ \rightarrow HOH$	1	1	−1	1/2	2/3	3/4	4/5
$O^{2-} + H^+ \rightarrow OH^-$	1	1	−2	1/3	1/2	3/5	2/3
$O^{2-} + 2H^+ \rightarrow HOH$	2	1	−2	2/3	1	6/5	4/3

*The orders were calculated using the equations:[2]

$$i_{M^{z+}} = k_{M^{z+}}^{n/\nu} \left(\frac{\beta_+ z_+}{\beta_+ z_+ - \beta_- z_-}\right) = i_{OH^-} = k_{H^+}^{n/\nu} \left(\frac{\beta_- z_-}{\beta_+ z_+ - \beta_- z_-}\right)$$

Table 4 gives the values of the formal orders of the reactions with respect to H^+ for different limiting stages. Eqn. (40) does not make it possible to explain the formal order of the reaction with respect to other ions (Fe^{2+}, Ni^{3+}, Cu^+, Mn^{2+}) influencing the rate of dissolution of the corresponding oxides. In the derivation of Eqn.(40) it was assumed that the quantity E is a compromise potential, and that reactions (21) and (22) are far from equilibrium. According to the experimental data, however, the potential jump should be regarded as quasi-equilibrium.

b) Determination of the formal order of a reaction with respect to the ions for the dissolution of metal oxides, on the basis of the proton theory. It is possible to find how the formal orders with respect to the ions change with change in the nature of the potential-determining reaction. If the magnitude of the potential

$$E = E^0 + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{RT}{F} \ln \left\{ \frac{[Fe^{3+}]}{[Fe^{2+}]} \exp\left(\frac{E^0 F}{RT}\right) \right\} \qquad (41)$$

of iron oxides is determined by the reaction $Fe^{3+} + e \rightarrow Fe^{2+}$, the rate of dissolution can be found by substituting Eqn.(41) in Eqn.(35) for $\beta_+ = 0.5$, $z_+ = 1$, $m = 0.5$:

$$\left(\frac{\partial \alpha}{\partial t}\right)_{sp} = k a_{H^+}^m a_{Fe^{2+}}^{(1-\beta_+)z_+} a_{Fe^{3+}}^{-(1-\beta_+)z_+} = k a_{H^+}^{0.5} a_{Fe^{2+}}^{0.5} a_{Fe^{3+}}^{-0.5} \qquad (42)$$

It follows from Eqn.(42) that the rate of dissolution of iron oxides increases with increase in the concentration of H^+ and Fe^{2+} ions (the formal order of the reaction with respect to Fe^{2+} is 0.5 ± 0.1, and that with respect to Fe^{3+} is −0.5 ± 0.1.[153] If the potential

$$E = E_x^0 + \frac{RT}{F} \ln (a_{H^+}^{x/(x-1)} / a_{Mn^{2+}}^{[2(x-1)]^{-1}})$$

is determined by the reaction

$$MnO_x + 2(x-1)e + 2xH^+ \rightarrow Mn^{2+} + xH_2O \qquad (43)$$

reversible with respect to metal and hydrogen ions, it follows from Eqns.(25) and (43) that¶

$$k_i = k a_{H^+}^{n - x(1-\beta_+)z_+/(x-1)} \cdot a_{Mn^{2+}}^{(1-\beta_+)z_+/2(x-1)}$$

The formal order of the reaction with respect to H^+ and Mn^{2+} ions depends on the stoichiometric composition of the oxide. For $x = 1.5$ in MnO_x, the formal order of the reaction with respect to H^+ is −0.5, and that with respect to Mn^{2+} is +0.5. For $x = 2.0$, the formal orders of the reaction with respect to these ions are +0.1 and +0.25 respectively. The rate of dissolution of the oxide depends on x, and the reaction rate constant has a minimum value for $x \cong 2$. Expressions for determining the formal order with respect to the ions H^+ and M^{z+} for other versions of the potential-determining reactions are given below:

$$\frac{x_2}{x_1 - x_2} MO_{x_1} + M^{z+} + ze \rightarrow \frac{x_1}{x_1 - x_2} MO_{x_2} \qquad (III)$$

$$MO_x + 2xH^+ + 2(x - z/2)e \rightarrow M^{z+} + xH_2O \qquad (IV)$$

Reaction	n_{H^+}	$n_{M^{z+}}$
(III)	m	$-\frac{(1-\beta_+)z_+}{z}$
(IV)	$m - \frac{(1-\beta_+)z_+ x}{(x - z/2)}$	$\frac{(1-\beta_+)z_+}{2(x-z/2)}$

c) The influence of the anionic composition of the electrolyte and complex formation on the specific rate of dissolution of oxides in acidic media and complexones. The addition of anions to an electrolyte and the formation of stable complexes increases the rate of the dissolution of metal oxides. The extraction of cuprite into H_2SO_4 is more rapid than that into $HClO_4$,[168] since the sulphate complex of copper(II) is more stable than the perchlorate complex. A study of the dissolution of α-iron(III) oxide in mineral acids[19,48] showed that the formal orders with respect to the anions are 0.72 for Cl^-, 0.35 for SO_4^{2-}, 0.30 for NO_3^-, and 0.02 for ClO_4^-. The rate of dissolution can be represented in the form:[19]

$$d[Fe^{3+}]/dt = k[H^+]^{0.5}[A^{z-}]^m$$

A study of the influence of EDTA and hydroxyethylidenediphosphonic acid (HEDP) on the rate of dissolution of iron and manganese oxides established that complex formation leads to an increase in the intensity of the process. The logarithm of the rate constant for the dissolution of Fe_3O_4 or Fe_2O_3 increases linearly with increase in the logarithm of the

¶ At a constant potential, $n_{H^+} = m$, and the order of the reaction with respect to Mn^{2+} is equal to zero. 0.

stability constant of the complex of iron(III) with the anion of the electrolyte.[19] This agrees with data obtained by other workers.[153,154,168]

The more rapid extraction of BeO [154] and dissolution of titanium minerals[169] in H_2SO_4, compared with hydrochloric acid, indicates that the anions influence the kinetics of these processes, and is due to the ability of the SO_4^{2-} anions to form more stable complexes with beryllium and titanium ions. The influence of anions on the potential and the rate of the dissolution of UO_2 has been discussed.[30] The rate of dissolution of the oxides NiO, Ni_2O_3, and CuO in complexones, which form stable complexes with metal ions, however, decreases with increase in the ligand concentration.

There are two approaches to the explanation of the influence of anions on the dissolution of metal oxides.

The mechanism of the conjugated influence of cations and anions. According to the theory proposed by Vermilyea,[12,72] the increase in the rate of the dissolution of oxides under the influence of anions and complex formation is due to an increase in the ease of removal of cations from the crystal lattice of the oxide, in accordance with equations reflecting both the adsorption and reaction of ligands with the metal ion:

$$[M(OH)_n]^{(z_+-n)+}(\text{solid}) + p\,A^{q-}(\text{ads}) \rightleftarrows [M(OH)_n(A^{q-})_p]^{(z_+-n-qp)+}(\text{solid})$$

and to the subsequent transfer of the resulting complex to the solution

$$[M(OH)_n(A^{q-})_p]^{(z_+-n-qp)+}(\text{solid}) \rightarrow [M(OH)_n(A^{q-})_p]^{(z_+-n-qp)+}(\text{aq})$$

where A^{q-} is an anion with charge $q-$, A^{q-}(ads) represents anions adsorbed on the oxide phase, p is the coordination number of the metal ion, and n the number of OH^- ions coordinated to the M^{z+} ion.

The dependence of the rate of dissolution of the oxide on the concentration of protons and anions for the complex

$$[M(OH)_n(A^{q-})_p]^{(z_+-n-qp)+}$$

according to Vermilyea[72] will be:

$$i = k a_{H^+}^{\frac{\beta_+(z_+-n-qp)}{\beta_+(z_+-n-qp)-\beta_-z_-}} \cdot a_{A^{q-}}^{-\frac{\beta_-z_-qp}{\beta_+(z_+-n-qp)-\beta_-z_-}} \qquad (44)$$

Eqn.(44) gives the theoretical order of the reaction with respect to H^+ and A^{q-} ions. The available published data are given in Table 5.

Vermilyea's theory has made it possible only to establish the relationship between the stability constant of the complex formed by the metal cation with the ligand and the rate of dissolution of the oxide. This theory requires further development, since there are experimental data which it does not explain.

1) According to Vermilyea's ideas,[19,48] the limiting stage of the process reduces to the removal of a cation from the lattice (that is when the values of E are displaced into the positive range, the rate of the dissolution of the oxide should increase), whereas it has been established experimentally† that the rate of the process is limited by the removal of oxygen (OH group) or by the introduction of a proton into the oxide phase (since a displacement of the potential into the cathodic range increases the rate of dissolution of most oxides).

2. For the oxides Fe_2O_3, Fe_3O_4, MnO_2, MnO, and Mn_2O_3, the addition of the corresponding cations (strong reducing agents, Fe^{2+}, Mn^{2+}) to the acid increases the rate of dissolution of the oxide phase,[31,160,166] which is not consistent with the theory being discussed, since the species adsorbed is not the anion (in accordance with Vermilyea's ideas), but the cation.[48]

3. The theory does not explain the decrease in the rate of the dissolution of manganese and iron oxides in acidic media when MnO_4^-, $Cr_2O_7^{2-}$, and other anions which are oxidising agents with respect to Fe^{2+} and Mn^{2+} ions respectively are added to the electrolyte.

4. The theory does not explain the decrease in the rate of the dissolution of various oxides (CuO, Cu_2O, NiO, Ni_2O_3) with increase in the concentration of Complexones (EDTA, HEDP).

5. In Vermilyea's opinion, a strong complex-forming reagent such as 1,10-phenanthroline should increase the rate of the dissolution of the oxide phase, whereas experimentally, a decrease in the rate of the dissolution of iron oxide (Fe_3O_4, Fe_2O_3) is observed when this reagent is added to the solution.

The electron–proton mechanism of the influence of anions and complex formation. According to this mechanism, the influence of anions and complex formation reduces to a change in the value of E for the oxide electrode. Since at the surface of separation between the phases the value of the potential is determined by the reaction

$$M^{z+}A + e \rightarrow M^{(z-1)+}A$$

it follows that displacements of the potential into the cathodic region and into the anodic region are observed, depending on the nature of the ligand A.

Table 5. Theoretical values of the orders of the reaction with respect to hydrogen ions (n_{H^+}), anions (n_{Aq^-}), and the species whose transfer limits the rate of dissolution of metal oxides.[12]

Oxide	n_{H^+}	n_{Aq^-}			
		ClO_4^-	Cl^-	SO_4^{2-}	NO_3^-
$Fe_2O_3 \cdot nH_2O$	0.50	0.02; $Fe(OH)_2^+$	0.72; $FeCl_2^+$	0.35; $FeSO_4^+$	0.30; $Fe(OH)NO_3^+$, $Fe(NO_3)_2^+$
$Cr_2O \cdot 3.6H_2O$	0.46	~0; $Cr(OH)_2^+$	0.27; $Cr(OH)Cl^+$, $CrCl_2^+$	0.29; $CrSO_4^+$	—
$NiO \cdot nH_2O$	0.56	~0; $NiOH^+$	—	—	—

† There is other evidence that the limiting stage reduces to the transfer of a proton to the oxide phase (see p.1048).

In aqueous EDTA solutions, the magnitude of the standard redox potential of the reaction $Fe^{III}(EDTA) + e \rightarrow Fe^{II}(EDTA)$ is +0.14 V,[170] whereas for the systems containing 1,10-phenanthroline, the value of E is +1.2 V (at pH 0).[171] These ligands form stable complexes with iron ions. It is assumed that $pK_{Fe^{II}L} = 14.26$, $pK_{Fe^{III}L} = 25.1$, and $pK_{Fe(phen)_3^{2+}} = 21.3$.

Experimentally, different effects are observed (with increase in the ligand concentration, an increase in the rate of the dissolution of the oxide is observed for EDTA, and a decrease is observed for 1,10-phenanthroline), proving that the potential of the medium plays a decisive role in the kinetics of the dissolution of the oxide phase.

The increase in the rate of the dissolution of iron oxide with change in the anion composition of the electrolyte in the order: $HClO_4 < HNO_3 < HBr < H_2SO_4 < HCl < H_3PO_4 < HF$ [19,53] is due to the change in the magnitude of the potential[153]

$$E = E^0 + \frac{RT}{F}\ln\frac{[Fe^{III}]_{total}}{[Fe^{II}]_{total}} + \frac{RT}{F}\left(\ln\frac{1}{\gamma_{ox}} - \ln\frac{1}{\gamma_{red}}\right)$$

of the reaction $Fe^{III}A + e = Fe^{II}A$, which limits the transfer of protons from the acid solution to the oxide (Fe_2O_3).[174] Substituting Eqn.(44) in Eqn.(35) shows that the rate of the dissolution of iron(III) oxide is given by an expression of the form

$$k_i = k a_{H^+}^{n_i} a_{Fe(II)}^{(1-\beta_+)z_+} a_{Fe(III)}^{-(1-\beta_+)z_+}\left[\sum_{n=0}^{q}(K_{red})_n[A]^n \Big/ \sum_{i=0}^{q}(K_{ox})_i[A]^i\right]^{-(1-\beta_+)z_+} \quad (45)$$

$$\frac{1}{\gamma_{ox}} = \sum_{i=0}^{q}(K_{ox})_i[A]^i;\ (K_{ox})_0 = 1;\ \frac{1}{\gamma_{red}} = \sum_{n=0}^{q}(K_{red})_n[A]^n;\ (K_{red})_0 = 1$$

where γ_{ox} and γ_{red} are the fractions of the iron(II) and iron(III) ions not combined in the complex, and K_{ox} and K_{red} are the stability constants of the complexes formed by the Fe^{3+} and Fe^{2+} ions respectively.

It follows from Eqn.(45) that for $z_+ = 1$ and $\beta_+ = 0.5$, the rate constant (k_i) is linearly dependent on the difference between the stability constants of the complexes of Fe^{III} and Fe^{II} with the anion of the electrolyte. The calculated values of the orders of the reaction with respect to the ions Fe^{2+}, Fe^{3+}, and H^+ agree with the experimental values. The experimental data obtained are given in Table 6.[153]

Complexones, which displace the stationary value of E into the cathodic range, facilitate the dissolution of oxides (Mn_2O_3, MnO_2, Fe_3O_4, Fe_2O_3, etc.). The greater the difference $(pK_{Fe^{III}(EDTA)} - pK_{Fe^{II}(EDTA)} = 10.74$ [175]), the greater the rate of the dissolution of iron oxide. The reason for the decrease in the rate of the dissolution of copper and nickel oxides with increase in the concentration of Complexones in the solution is that these ligands displace the potentials of the oxide electrodes into the cathodic range. To increase the rate of the dissolution of these oxides, it is necessary to displace the potential into the anodic range. The electron–proton mechanism makes it possible to explain all the experimentally observed regular kinetic features of the dissolution of metal oxides.

4. The Influence of the Preparation of the Specimen and the Experimental Conditions

The kinetics of the dissolution of oxides are influenced by the method used to prepare the specimens,[176] the nature of the defects,[107] the state of the surface,[177] and the adsorption of ions from the solutions.[107] The dissolution of NiO in sulphuric acid shows an induction period,[107] the duration of which increases with increase in the time for which the specimen is kept in air, and this can be related to a change in both the quantity of defects and the electrical conductivity of the specimen. With increase in the oxygen pressure, the induction period for the dissolution of nickel(II) oxide decreases, due to an increase in the number of Ni^{3+} vacancies. In the dissolution of the oxides of copper, iron, and nickel, the addition of oxidising agents (MnO_4^-, $Cr_2O_7^{2-}$) and reducing agents (Fe^{2+}, I^-) to the electrolyte solution changes the duration of the induction period.[31,109,176] In the presence of these ions, which show oxidising properties in an acidic medium, the concentration of the defects (Ni^{3+}) in NiO decreases. The sites corresponding to the intersection of dislocations on the surface of the crystals represent the centres at which the dissolution process begins. The rate of the dissolution of NiO and Fe_2O_3 decreases with increase in the temperatures at which the specimens are heated from 700 °C to 1000 °C, since thermal treatment decreases the number of defects and leads to a decrease in the effective surface area of dissolution.[107,178,179]

The anisotropy of the dissolution of metal oxides. Polycrystalline specimens are characterised by orientational non-uniformity of the properties, so that a change in the nature of the kinetic curve with time is sometimes related to the non-uniformity of the dissolution of the surface of the specimen. This situation is observed in the dissolution in acid of TiO_2,[180] FeOOH,[181] Fe_2O_3,[182,183] and Al_2O_3.[184] Each plane of α-Al_2O_3 crystals is characterised by a definite form and orientation of the etch pits.[185]

The basal plane (0001) of α-Al_2O_3 and α-Fe_2O_3 is extracted into acids much more rapidly than the other planes.[4] The etch figures are determined by the crystal defects, depend on the anion composition of the solution and on the nature of

Table 6. Dependence of the kinetic parameters of the dissolution of iron(III) oxide on the nature of the acid (at 50 °C).

Acid	$t_{0.5}$, min	α_{max}	$E_{Fe(III)A/Fe(II)A}$, V (Ref.174)	Eqn. (46)	Eqn. (48)			
				$10^7 k_i$, cm min^{-1}	$10^7 k_i$, cm min^{-1}	$10^{-2} k_g$, cm^{-2}min^{-1}	$10^{-3} A$	$\tau_{0.5}$
HF	246	0.25	0.55	126	103.7	122.30	5.0	0.17
H_3PO_4	360	0.12	0.59	86	33.3	49.49	63.0	0.08
HCl	522	0.15	0.64	59.3	28.7	21.67	32.0	0.10
H_2SO_4	1 860	0.21	0.68	16.6	11.3	2.67	10.0	0.14
HBr	4 200	0.30	0.75	7.4	7.9	0.37	2.0	0.22
$HClO_4$	30 000	0.15	0.78	1.03	0.5	0.38	32.0	0.10

Note. $t_{0.5}$ is the time required for the dissolution of half of the oxide specimen; the rate constant (k_i) according to Eqn.(42) was calculated for 1 M acid solutions; $\tau_{0.5}$ is a quantity proportional to the time taken for the reaction to proceed to the extent $\alpha = 0.5$ ($\tau_{0.5} = k_i t_{0.5}$).

the acid, and show different geometries, depending on the orientation of the face.[4] The rate of the dissolution of a polycrystalline specimen depends on the relationship between its dimensions and the magnitude of the granules of which it is made up.[186] The chemical etching of crystals has established[187,188] that there is an increased reactivity at the dislocation sites. Studies carried out in this direction have been reviewed.[126]

5. Dependence of the Nature of the Dissolution on the Character of the Chemical Bond in Oxides and on the Presence of Additives

The processes associated with the dissolution of oxides (see Fig. 3) can be divided into three classes:[2]

1) non-oxidative dissolution (BeO, CdO, Al_2O_3);

2) the dissolution of oxides (CuO, NiO, UO_2) accelerated by oxidation processes[30,107–110] and anodic polarisation;[30, 107,110]

3) the dissolution of oxides (Fe_2O_3, MnO_2) accelerated by reduction processes[31] and cathodic polarisation.[152]

The dissolution of metal oxides in acids is a multi-stage process. The limiting stage may be a solid-phase process[189,190] or a reaction in the electrolyte solution (as shown for zinc oxide[191]). In an oxide with ionic bonds, the dissolution takes place by a solid-phase mechanism. The transfer of ions to the electrolyte solution in this case takes place without a change in the oxidation state of the cations and anions. The presence of additives and impurities in these oxides has little influence on the rate of their dissolution. The addition of the oxides Li_2O or Al_2O_3 to ZnO does not change the rate of their dissolution in HCl.[192]

In oxides with more covalent bonding, the presence of additives influences the rate of dissolution. The addition of Li^+ ions to NiO leads to an increase in the rate of the dissolution of the specimen, due to an increase in the electrical conductivity of this oxide.[107,149,193] The increase in electrical conductivity[193,194] leads to an increase in the exchange current of the potential-determining reaction and an increase in the rate of the diffusion of H^+ into the oxide. A similar effect is observed when Ti^{4+} ions are added to Fe_2O_3.[193]

For the dissolution of ionic crystals (BeO, ZnO) in H_2SO_4, the properties of the solution play a more important role than the properties of the solid phase. In the dissolution of covalent oxides, the structure of the solid phase (volume charge, different surface states, and also specific adsorption) determines the chemistry of the dissolution.

6. Influence of the Temperature of the Electrolyte on the Rate of the Dissolution of Oxides

The study of the influence of temperature on the dissolution of oxides in acids has established that the rate of the dissolution increases considerably with increase in the temperature of the electrolyte. The activation energy of the process reaches ~80–90 kJ mole^{-1} (see Table 7), which coincides with that obtained for the solid-phase reduction of iron oxides using H_2, CO, and other reagents as reducing agents.[206,207] The order of magnitude of these quantities is close to that of the activation energy of the diffusion of a proton into the oxide phase.[208] The high activation energy of the dissolution is due to heterogeneous processes whose limiting stage lies in the kinetic range.[20,31,153,209] The nature of the limiting stage remains unchanged with increase in the temperature of the electrolyte.

VII. MODELS DESCRIBING THE CHANGE IN THE SURFACE AREA OF THE DISSOLVING PARTICLE

The increase in the rate of the dissolution of oxides with time is attributed to a change in the magnitude of the surface area of the specimen as a result of etching. For the interpretation of the change in the kinetics of the process with time, it is possible to put forward a number of models which

Table 7. Effective activation energies (E_a, kJ mole^{-1}) of the dissolution of metal oxides in acid solutions.

Oxide	Acid	E_a	Oxide	Acid	E_a	Oxide	Acid	E_a	Oxide	Acid	E_a
Fe_2O_3	HCl	95.8 [4]	Fe_2O_3	H_2SO_4	91.6 [19]	Fe_2O_3	HNO_3	76.1 [19]	Fe_2O_3	$HClO_4$	80.3 [19]
NiO	HCl	72.0 [109]	Ni_2O_3	HCl	70.3 [109]	Fe_2O_3	HCl	113.0 [162]	Cu_2O	H_2SO_4	54.4 [163]
Cu_2O	H_2SO_4	96.2 [163]	CuO	H_2SO_4	54.4 [163]	CuO	H_2SO_4	96.2 [163]	Ni_2O_3	H_2SO_4	143.5 [176]
Fe_2O_3	HCl	90.4 [180]	Fe_2O_3	$HClO_4$	87.0 [180]	Fe_2O_3	HCl	41.8 [195]	Fe_2O_3	H_2SO_4	53.6 [195]
Fe_2O_3	HNO_3	44.4 [195]	Fe_2O_3	H_2SO_4	87.9 ± 4.2 [196]	Fe_2O_3	HF	51.5 [197]	TiO	H_2SO_4	62.8 [198]
Ti_2O_3	H_2SO_4	87.9 [198]	Ti_3O_5	H_2SO_4	75.3 [198]	Al_2O_3	HCl	47.3 [199]	Al_2O_3	HNO_3	47.7 [199]
Cr_2O_3	HF	43.1 [199]	Cr_2O_3	H_2SO_4	47.7 [200]	Cr_2O_3	8 *M* H_2SO_4 + + 40% acetone	35.1 [200]	ZnO	HCl	37.8 [201]
Mn_2O_3	H_2SO_4	78.7 [202]	NpO_2	$HClO_4$	77.0 [203]	UO_2	H_2SO_4	75.3 [204]	$TiO_{0.8}$	H_2SO_4	75.7 [205]
$TiO_{0.8}$	H_2SO_4	72.0 [205]	$TiO_{0.8}$	H_2SO_4	56.9 [205]	$TiO_{0.8}$	H_2SO_4	55.6 [205]	$TiO_{0.9}$	H_2SO_4	89.1 [205]
$TiO_{0.9}$	H_2SO_4	65.7 [205]	$TiO_{0.9}$	H_2SO_4	55.6 [205]	$TiO_{0.9}$	H_2SO_4	92.5 [205]	$TiO_{0.9}$	H_2SO_4	49.0 [205]
$TiO_{0.9}$	H_2SO_4	77.0 [205]	$TiO_{1.0}$	H_2SO_4	85.4 [205]	$TiO_{1.0}$	H_2SO_4	80.8 [205]	$TiO_{1.0}$	H_2SO_4	55.2 [205]
$TiO_{1.0}$	H_2SO_4	49.0 [205]	$TiO_{1.1}$	H_2SO_4	159.0 [205]	$TiO_{1.1}$	H_2SO_4	80.8 [205]	$TiO_{1.1}$	H_2SO_4	61.5 [205]
$TiO_{1.1}$	H_2SO_4	59.8 [205]	$TiO_{1.2}$	H_2SO_4	190.4 [205]	$TiO_{1.2}$	H_2SO_4	79.5 [205]	$TiO_{1.2}$	H_2SO_4	60.7 [205]
$TiO_{1.2}$	H_2SO_4	98.3 [205]	$TiO_{1.3}$	H_2SO_4	63.6 [205]	$TiO_{1.3}$	H_2SO_4	94.6 [205]	—	—	—

Note. Numbers in square brackets denote references (Ed. of Translation).

describe the development of the reaction front during the reaction of the specimen with the electrolyte and which make it possible to determine the explicit form of the function $f(\alpha)$ (1). It is of interest to discuss the general regular features of the dissolution of oxide particles when they are present continuously in the suspended state in the reaction vessel and are subjected to the action of the electrolyte. The change in the surface area during the dissolution of oxides is described by different relationships, depending on the original geometry of the specimens. If the original oxide can be represented in the form of a flat plate (electrode), and its dissolution takes place uniformly, the fraction of dissolved substance will change linearly with time: $\alpha = k_i t / r_0$.

The explicit form of this function has not yet been established for the case where the magnitude of the surface changes non-uniformly during the dissolution.

If the particle has a spherical shape, the time dependence of the fraction of the dissolved oxide will be described by the following equations:

$$1-(1-\alpha)^{1/3}=\frac{k_i t}{r_0};\ \frac{\partial\alpha}{\partial t}=(k_i/r_0)(1-\alpha)^{2/3} \qquad (46)$$

These equations were derived with the assumption that uniform dissolution of the particle takes place; usually, however, the dissolution of the particles of the oxide specimen is non-uniform. One of the formal heterogeneous models which shows the development of a non-uniform reaction front during the reaction of a particle with an acid is described below.

Kinetic theories of the dissolution of oxides taking account of the formation of active centres on the surface of spherical oxide phases are based on the applicability of the mathematical apparatus proposed by Delmon and Mampel.[210] According to this theory, the rate of dissolution is determined by two parameters: the rate constant for the production of nuclei, that is the active centres of the dissolution (k_g), and the rate constant for their dissolution (k_i). A relationship between α and t has been proposed.[210] The volume of a spherical particle with radius r_0 is equal to the sum of the volumes of layers which have a thickness dx and which are situated at a distance x from the surface. The volume of one dissolving layer is $\beta(x, t)$ and represents the sum of the dissolved volumes of each sphere, divided by the original volume $\frac{4}{3}\pi r_0^3$:

$$\alpha=\int_0^{r_0}\frac{3(r_0-x)^2}{r_0^3}\beta(x,t)\,dx=\frac{3}{r_0}\int_0^{r_0}\left(1-\frac{x}{r_0}\right)^2\beta(x,t)\,dx \qquad (47)$$

From the theory of heterogeneous kinetics, the value of $\beta(x, t)$ will be determined by the Poisson relationship[211]

$$\beta(x,t)=1-\exp(-S\gamma)$$

where $\gamma = r_0^2 k_g/(r_0 - x)^2 = N(\theta, x)$ is the number of dissolution centres produced on the surface of spheres with radius $(r_0 - x)$ at moment of time θ; and

$$S=\pi\left(\frac{r_0-x}{r_0}\right)[k_i^2(t-\theta)^2-x^2]$$

is the surface area of a dissolved segment with radius $(r_0 - x)$. Using the new parameters

$$A=4\pi r_0^3 k_g/k_i;\ \tau=k_i/r_0 t;\ \xi=x/r_0$$

Eqn.(47) can be reduced to the form:

$$\alpha=1-(1-\tau)^3-3\int_0^{\tau}(1-\xi)^2\exp\left(-\frac{A}{12}\,\frac{\tau^3-3\xi^2\tau+2\xi^3}{1-\xi}\,d\xi\right) \qquad (48)$$

Eqn.(48) does not have an analytical solution. The kinetic parameters are calculated using the tabulated values of this function for different values of τ and A.[210] The calculation of the quantities k_i and k_g reduces to the determination of $\tau_{0.5}$, A, and $t_{0.5}$. The determination of A reduces to the superposition of the graph of the experimental data, constructed on coordinates $\alpha - (t - t_l)/(t_{0.5} - t_l)$, on the network of theoretical curves (on the same coordinates) for different values of A. The value of A (tabulated values[210]) is used to find $\tau_{0.5}$ for $\alpha = 0.5$.[210] The values of k_i and k_g are determined using the equations

$$k_i=r_0\frac{\tau_{0.5}}{t_{0.5}-t_l};\ k_g=Ak_i/4\pi r_0^3$$

Usually, k_i is much smaller than k_g, that is the process is limited by the rate of the dissolution of each active centre. As $A \to \infty$, the dependence of α on t is described by the expression used to analyse the kinetics of the dissolution of oxides:

$$1-(1-\alpha)^{1/3}=k_i t/r_0$$

The proton theory of dissolution, taking account of the formation of active nuclei in the volume of spherical oxide particles. To explain the anomalously rapid dissolution of oxides, there is another theory, according to which an increase in the number of active centres (nuclei) in the volume of an oxide takes place as a result of diffusion of H atoms.[166] During dissolution, filamentary branching of the nuclei is observed in a direction perpendicular to the surface of the specimen. Two stages of the process are distinguished: the production of the nuclei and their dissolution.[166,212] In front of the moving surface of the oxide/electrolyte interface there are nuclei (N_0) whose activation requires that they react with the adsorbed hydrogen diffusing from the surface of the oxide phase. The active centres are usually formed at dislocation sites. The hydrogen atoms can diffuse along the dislocations into neighbouring centres, forming new active centres (N).[212] These assumptions agree with data on the adsorption of protons and their subsequent diffusion into the volume of an oxide phase, and with the ideas developed by Lukovtsev and co-workers.[120]

The relationship between α and t was found from the following considerations:

a) the rate of formation of the nuclei $(\partial N/\partial t)_\theta$ is directly proportional to the product of the number of potential centres $(N_0 - N)$ existing at a given moment of time θ and the apparent degree of transformation, with allowance for their overlap and absorption (αf):[213]

$$\partial N/\partial t=k(N_0-N)\alpha_f=-k(N_0-N)\ln(1-\alpha) \qquad (49)$$

where αf is related to the actual degree of transformation α (in accordance with the Poisson equation) by the relationship

$$\alpha_f=-\ln(1-\alpha)=\int_0^t S(\theta,x)N(0,x)\,d\theta$$

where $N(\theta, x)$ is the number of active centres on unit surface area of the sphere (at moment of time θ), observed at a depth x from the surface of the oxide; and $S(\theta, x)$ is the size of the segment cut out by the active centre in the sphere situated on the oxide surface;

b) the rate of dissolution of oxides is directly proportional to the product of the number of active centres and the unreacted fraction of the oxide $(1 - \alpha)$ (and not simply $\partial\alpha/\partial t = kN$, as given by Prout and Tomkins):[214]

$$\partial\alpha/\partial t = kN(1-\alpha) \quad \text{or} \quad \partial\alpha_f/\partial t = k_1 N \tag{50}$$

Assuming that the potential centres are in a large excess, Eqns.(49) and (50) can be used to find α_f:

$$\partial\alpha_f/\partial t = kN$$
$$\partial N/\partial t = k_1 N_0 \alpha_f \quad \text{or} \quad \partial^2\alpha_f/\partial t^2 - k_1 k N_0 \alpha_f = 0 \tag{51}$$

The solution of the differential equation (51) is the function

$$\alpha_f = A \operatorname{sh} k_i t$$

This gives an equation of the form:

$$-\ln(1-\alpha) = A \operatorname{sh}(k_i t); \; \partial\alpha/\partial t = A k_i (1-\alpha)[A^2 + \ln^2(1-\alpha)]^{1/2} \tag{52}$$

where $k_i = (k_1 k N_0)^{1/2}$.

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The quantitative comparison, carried out in the present review, of the factors influencing the rate of the dissolution of metal oxides in acids has revealed the decisive role of the proton and electron concentration gradients (potential) on the kinetics of this process. The knowledge of the kinetics and mechanism of the dissolution of oxide phases has now reached a state in which future progress will depend on obtaining further details of the description of electrochemical processes at the oxide/solution interfaces.

The mechanism of the dissolution of a metal oxide and the nature of the limiting stage have still been insufficiently studied. The classical theories of the dissolution of ionic crystals require further development, since they do not yet make it possible to explain the influence of complexones on the kinetics of the dissolution of semiconducting oxides (CuO, NiO, Ni_2O_3, and other oxide specimens); moreover, for the great majority of metal oxides, the nature of the potential-determining reactions at the surface of separation between the solid and liquid phases has not yet been explained.

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Lenin Moscow State
Pedagogic Institute
Soviet Trade Correspondence
Institute, Moscow

Translated from *Uspekhi Khimii*, 53, 1827-1851 (1984) U.D.C. 541.64 : 536.7

Phase Equilibria and Mutual Diffusion in Polymer—Polymer Systems with Chlorine-containing Components

A.E.Chalykh and I.N.Sapozhnikova

The experimental studies of the phase equilibria and mutual diffusion in polymer mixtures are examined. A thermodynamic analysis of the phase equilibria in the poly(vinyl chloride)-poly(methyl methacrylate) and chloropolyethylene-poly(methyl methacrylate) systems is presented within the framework of classical and new theories; the influence of the previous history of the specimens and of the chemical structure and stereoregularity of the polymer chains on the phase composition of the mixtures is demonstrated. The translational mobility of the macromolecules in the highly elastic and highly fluid states and its role in the formation of the phase structure of the mixtures and also the irreversible changes in the phase structure on thermal decomposition of chlorine-containing polymers are considered.
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I. INTRODUCTION

The interest in the problem of the compatibility of polymers is due to the need to create new polymeric materials and procedures including the blending of polymeric components. There exist nowadays extensive data whose analysis makes it possible to determine the principal trends in the research into polymer blends: the empirical search for materials with specified properties, the study of the thermodynamics of the blending of polymers, analysis of the colloidal-chemical properties of disperse systems, the study of the compatibility of various polymer pairs, and the search for new research techniques and new criteria of compatibility.

A single physicochemical approach to the analysis of polymer blends, which requires information about the equilibrium phase structure and kinetic characteristics of the systems, namely the diffusion coefficients, the decomposition constants of the components, etc., which would make it possible to predict the changes in the properties of polymer blends during their preparation, use, and storage, is particularly important. The neglect of this approach and methodological difficulties lead to the accumulation of contradictory information concerning the compatibility of polymers, which is frequently useless from the standpoint of practical employment. The difficulty of determining diffusion coefficients for polymer blends is associated with the low translational mobility of the macromolecules in a medium comprising similar molecules and the scope of the integral methods used nowadays for the determination of the compositions of the coexisting phases is extremely limited, because these methods require prolonged isothermal annealing in order to attain equilibrium throughout the bulk of the blend, which is not always attainable owing to the thermal decomposition of the components.

The present level of the development of local analytical methods with high resolution makes it possible to revise the methodology of the approach to studies of this kind, because in local contact regions the times required for the attainment of equilibrium have a significantly different scale. During the last five years, a local X-ray microanalytical method combined with scanning electron microscopy has been developed and used in the combined study of the parameters of mutual diffusion, thermal stability, and phase equilibria in polymer—polymer (P—P) systems. The pronounced "localisation" of the method ensures that the equilibrium isothermal annealing is carried out during sufficiently short periods and makes it possible to investigate any P—P systems before the onset of intense thermal decomposition and also to trace its influence on the phase structure of the blend. Such studies have been carried out in relation to systems with chlorine-containing components: poly(vinyl chloride) (PVC)—poly(methyl methacrylate) (PMMA), chloropolyethylene (CPE)—PMMA, and certain others; the phase diagrams and the diffusion constants have been obtained and the influence of the thermal decomposition of the components and the previous history of the blends on these parameters has been examined.

The aim of the present review is the analysis of the characteristic features of the phase equilibria and the mutual diffusion in polymer blends based on experimental results obtained with the aid of the local analytical methods for systems with chlorine-containing components and also the examination of the prospects which arise as a consequence of the application of these methods to the experimental solution of the problem of the compatibility of polymers.

II. THE STATE OF RESEARCH INTO PHASE EQUILIBRIA IN POLYMER—POLYMER SYSTEMS

A characteristic feature of polymer solutions is the slow attainment of equilibrium in phase separations. Even for polymer—low-molecular-weight solvent (P—S) systems, complete phase separation with formation of a single interface is not always attained;[1] this applies even more to P—P systems. Polymer blends are therefore frequently obtained

and used under conditions far from equilibrium. Nevertheless phase diagrams actually determine the structural-morphological characteristics of the structure of the materials and the trends in the variation of the properties during prolonged use. The analysis of the phase equilibrium is therefore a task of primary importance for the practical selection of the specified materials, for the determination of the conditions of their processing and storage, etc.

Until recently phase equilibria in P–P systems have been discussed solely in theoretical terms. Within the framework of the classical theories (the Hildebrand, Flory–Huggins, Tompa, and Scott theories), the miscibility is limited from above as regards molecular weight. Indeed the positive combinatorial entropy ($\Delta S_{comb} > 0$), which is related to the number of species per unit volume and which determines the entropy of mixing (ΔS_{mix}) in the Flory–Huggins–Scott lattice model, diminishes with increasing molecular weight (MW) of the components. Consequently the positive enthalpy of mixing (ΔH_{mix}), for which phase separation takes place, also diminishes with increasing MW. The incompatibility of polymeric components has been for a long time thought to be a general phenomenon precisely from these standpoints.[2,3] However, the Flory–Huggins–Scott theory is not universal; it does not take into account the concentration and temperature dependences of the interaction parameter χ_{12} and the non-combinatorial entropy contribution to ΔS_{mix} and accounts for the phase equilibrium only in those systems which are characterised by an upper critical solution temperature. This theory has received a number of improvement designed to take into account the volume changes occurring on mixing of the components and responsible for the discrepancy between the theory and the behaviour of solutions. Thus Flory divided χ_{12} into the enthalpy (χ_H) and entropy (χ_S) components. The determination of these quantities for polymer–solvent systems made it possible to explain many phenomena occurring in polymer solutions.[4] Evidently, the determination of these parameters also for P–P systems should be very important for the understanding of the thermodynamics of phase equilibria in polymer blends.

In modern theories constructed on the basis of Prigogine's general theory of corresponding states, the properties of mixtures are expressed in terms of the characteristic parameters of state of the pure components: pressure, volume, and temperature. This applies primarily to Flory's new theory, Patterson's theory, and the lattice theory of Sanchez and Lacombe. These theories take into account the influence of the structure and properties of the components on the properties of the mixture and make it possible to explain the phenomenon of both the upper and lower critical solution temperatures of polymers. Fig.1 illustrates the possible types of phase diagrams of P–P mixtures which obtain in calculations over narrow limits of variation of the parameters of the equation of state.[5]

On the basis of the new theory, Flory calculated the changes ΔH_{mix} and ΔS_{mix} on blending polyisobutylene and polymethylene in the liquid state and found that the free energy of mixing is positive ($\Delta G_{mix} > 0$) over the entire range of compositions, which indicates the incompatibility of the above polymers.[6] However, calculations of this kind involve certain difficulties owing to the large amount of labour involved in the experimental determination of the parameters of the equation of state. Only individual attempts at a general theoretical analysis of the phase equilibria of polymer mixtures on the basis of the theory have therefore been made so far. Thus McMaster[7] used modified equations of Flory's new theory to calculate the phase diagrams of P–P blends. We carried out calculations for two types of hypothetical systems. The first was selected with the maximum possible difference between the parameters of the equations of state of the components and the second was selected with identical parameters with the exception of the coefficient of thermal expansion α. The chain length, the degree of polydispersity, the pressure, and the coefficient of thermal expansion were varied alternately. For $X_{12} = Q_{12} = 0$, the phase equilibria are characterised by a lower critical solution temperature (LCST) (the values of X_{12} and Q_{12} characterise the difference between the interaction energies between identical and non-identical pairs of segments and the change in the entropy of interaction of neighbouring segments respectively). It has been shown that LCST decreases with increasing molecular weight and increases with increasing pressure; similar values of α for components 1 and 2 improve their compatibility. Whereas the presence of the LCST is characteristic in cases where $X_{12} \leqslant 0$, when $X_{12} > 0$ an upper critical solution temperature (UCST) appears together with the LCST. For high positive values of X_{12}, the diagrams assume an hour-glass form. The fulfilment of the condition $Q_{12} \neq 0$ also leads to the presence of the UCST. It is striking that the UCST has been observed over a very narrow range of values of X_{12} (from 0.005 to 0.001). The conclusion, which had a major influence on the course of further studies, namely that an equilibrium with a LCST is typical for P–P systems, was in fact reached on this basis.

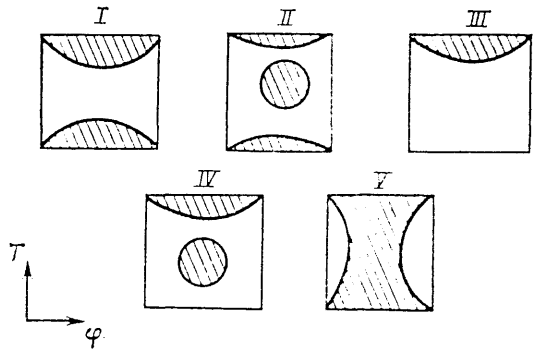


Figure 1. Schematic representation of "temperature–composition" (T–ϕ) phase diagrams predicted by the theory of the equation of state for P–P systems.[5]

However, it is noteworthy that the task is at present experimental rather than theoretical: the aim is to discover which values of the thermodynamic parameters are characteristic of P–P systems and which type of phase equilibrium is most typical for such systems. In calculations on hypothetical systems, the universality of the theory makes it possible to obtain any of the diagrams illustrated in Fig.1 subject to certain assumptions. Thus the hypothesis that $X_{12} \leqslant 0$ and $Q_{12} = 0$ (McMaster[7]) rules out the UCST version and leads to diagrams of type III (Fig.1).

The temperature dependence of X_{12} has been analysed[8] within the framework of the above theory. The following expression has been obtained:

$$\frac{\chi_{12}}{M_1 V_1^*} = \frac{P_1^*}{RT}\left[\underbrace{\frac{\tilde{V}^{1/3}}{(\tilde{V}^{1/3}-1)}\left(\frac{X_{12}}{P_1^*}\right)}_{A} + \underbrace{\frac{\tilde{V}^{1/3}}{2(4/_3-\tilde{V}_1^{1/3})}\cdot\tau^2}_{B}\right], \qquad (1)$$

where the quantities marked by an asterisk are characteristic parameters and those marked by a bar are reduced parameters; $\bar{V} = V/V^*$, $\bar{T} = T/T^*$, $\bar{P} = P/P^*$, $\tau = 1 - T^*/T_2^*$, and M_1 is the molecular weight of the segment. The reduced volume can be expressed in terms of the coefficient of thermal expansion:

$$\bar{V}_1^{1/3} = 1 + \frac{\alpha T}{3(1+\alpha T)}. \qquad (2)$$

Eqn.(1) shows that the χ_{12} comprise two contributions: the contribution of the term describing the interaction of a pair of segments (the first term A) and the contribution of the term describing the change in free volume on mixing the segments (the second term B). It follows from Eqns.(1) and (2) that, when $\alpha \to 0$, then $\bar{V}_1^{1/3} \to 1$ and $A \to \infty$; on the other hand, when $\alpha \to \infty$, then $\bar{V}_1^{1/3} \to 4/3$ and $B \to \infty$. The values of $\bar{V}_1^{1/3}$ quoted[8] for polymers and low-molecular-weight liquids and the results of the calculations show that the role of the free volume in the miscibility of polymers is significantly smaller than in P–S systems and smaller than the values obtained in McMaster's calculations. It has been shown that the appearance of a LCST higher than the UCST in P–P systems is theoretically impossible owing to the free volume effects, since τ should then increase to values unacceptable for the thermal stability of P–P systems.

Flory's new theory and its modifications provide criteria for the search for and the determination of compatible polymer–polymer systems. It is assumed that the conditions under which we have simultaneously $T_1^* > T_2^*$ and $P_1^* > P_2^*$ are the most favourable for the compatibility of polymers and the values of T_1^* and T_2^* themselves should not differ by more than 200 K. (Subscripts 1 and 2 correspond to the individual components.) One of the most evident criteria of Flory's new theory is the parameter X_{12}. A negative value of X_{12} implies that the polymeric components are characterised by the so-called specific interaction and the phase equilibrium has a LCST. However, it has been noted[8,9] that the case where $X_{12} < 0$ (i.e. $\Delta H_{mix} < 0$) can be abolished when $Q_{12} < 0$ ($\Delta S_{mix} < 0$), as has been shown for certain polymer–solvent systems;[4] this creates difficulties in the prediction of the types of equilibrium for P–P systems.

Thus, despite the fact that the theories mentioned are universal and provide criteria for the prediction of the compatibility of the components of the blend, they have still not been adequately analysed and so far have been interpreted in different ways. In addition, a much wider comparison between the conclusions reached in terms of different theories and experiment is necessary in order to reach a conclusion concerning the superiority of a particular theory in describing the behaviour of polymer blends and to ensure the possibility of predicting the phase equilibria by means of analytical methods.

Topological analysis based on comparison of the positions of the phase transition regions has been recently applied to P–P blends with alternating molecular weights of the components (block-copolymers).[10] This analysis provides an estimate of the general type of phase diagrams but does not determine the quantitative miscibilities of the components, which can only be obtained experimentally.

Any properties characterising the homogeneity of the system for different compositions (the intensity of the low-angle, optical, X-ray, electronic, or neutron scattering and the glass point) or the thermodynamic characteristics (free energy of mixing, enthalpy of mixing, the solubility parameter, the interaction parameter, and the specific heat) are used as experimental criteria of compatibility. As a rule, there is no agreement between the limits of compatibility found from these criteria within a single system; this is illustrated by Table 1.

A similar discrepancy can be observed also on comparing the experimental data for the compatibilities of many other pairs of polymers.[2,16] Attention has been frequently drawn to be discrepancies between the experimental results and specific causes of incompatibility have been discussed in the literature.[12,15,17] From our point of view, this situation can be accounted for by the limited nature of the criteria employed and also of the methods of their determination. Thus the compatibility data obtained by direct measurements of any parameter characterising the homogeneity of the system are limited and uncertain as regards temperature. In all probability, the information obtained refers to the temperature of the mixing of the components. The thermodynamic characteristics measured in binary systems using a third component, namely the solvent (for example, ΔG_{mix} determined by the method of Hess's cycle or χ_{12} obtained by the method of reverse gas chromatography or neutron scattering[18–20]), are also functions of the initial state of the system and cannot serve as criteria of the existence of a true equilibrium.

Table 1. The compatibility of PVC and PMMA.

Research method	Conditions of contact	$10^{-4}M_{PVC}$	$10^{-4}M_{PMMA}$	ω_1''	ω_2'	Refs.
I	Welding (433–443 K)	—	—	*	*	[11]
I	From solution in THF	8	10.7	0.02	0.06	[12, 13]
I	Ditto	23	49.3	0.01	0.05	[12, 13]
I	From melt	8	10.7	0.05	0.55	[12, 13]
I	Polymerisation of MMA in PVC	—	—	0.05	0.50	[12, 13]
II	From solution in THF	10.7	9.9	0.30	0.20	[14]
II	From melt (423–433 K)	10.7	9.9	0.20	0.20	[14]
III	From solution in DMF	5.5	8.0	—	0.60	[15]
IV	From solution in 2-butanone	5.5	8.0	**	**	[94]

Notation. Methods: I) electron microscopy; II) thermodynamic method (method based on Hess's cycle); III) determination of the glass point T_g by differential scanning calorimetry; IV) determination of the phase separation from turbidity points; ω_1'' and ω_2'—weight fractions of PVC in PMMA and of PMMA in PVC respectively determined as compatibility limits.

*Incompatible.

**Fully compatible.

An experimental criterion characterising the miscibility of the components may be the phase composition of the system determined over a wide temperature range under conditions close to equilibrium. The determination of the true phase diagrams for P–P systems is a complex task. Classical methods,[21] involving homogenisation and prolonged thermal annealing, are not always suitable for this purpose owing to the high viscosity and low thermal stability of polymers. In order to obviate these difficulties, the mixtures are prepared as a rule in an effective solvent with its subsequent removal. However, it has been shown[22] that in this case the limits of the miscibility depend on the "quality" of the solvent. They characterise the phase equilibrium in a three-component P–P–solvent system established during the formation of the mixture and corresponds to a non-equilibrium state of the binary system in the absence of a solvent. Fig.2 illustrates the variation of ω_1'' for the PVC–PMMA system obtained in "good" (dichloroethane, $\chi_{PVC} = 0.428$) and "poor" (benzene, $\chi_{PVC} = 0.77$) solvents with isothermal annealing. Evidently the equilibrium values of ω_1'' attained during annealing are higher than for the system obtained from the "poor" solvent and lower than the values found using the "good" solvent.

The accumulation of a large amount of contradictory information concerning the miscibility of polymers is probably in fact to a large extent associated with the previous history of the specimens. Unfortunately, the accumulation of contradictory information has not ceased even when the method of turbidity points, traditionally used to study P–S and polymer–oligomer (P–O) systems, was used to construct phase diagrams.[1]

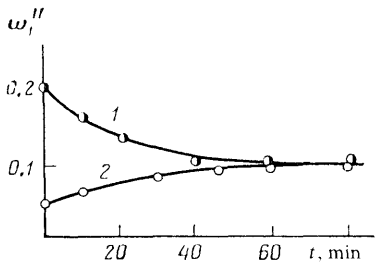


Figure 2. Variation of the limit of the compatibility of PVC and PMMA during annealing at 413 K for blends prepared from solution in DCE (curve *1*) and in benzene (curve *2*).[44]

Table 2. The phase equilibria in P_1–P_2 systems determined from turbidity points.

P_1	P_2	$10^{-4}\cdot M_1$	$10^{-4}\cdot M_2$	T_c, K	Refs.
PS	PMVE	1—20	5.1	LCST, 393-473	[23, 24]
PS	PMVE	—	—	LCST, 353; UCST, 303	[25]
PC	P-ε-CL	2.9	4.0	LCST, 533-546	[26]
PSAN (AN 28%)	PMMA	22.3	9.2	LCST, 233	[27]
PVC	PEVA (VA 63%)	—	12.5	LCST, 460-470	[28]
PVF	PMA	19.7	—	LCST, 563	[27, 29]
PVF	PEA	19.7	—	LCST, 333	[27, 29]
PVF	PMVK	19.7	—	LCST, 473	[29]
PVF	PEMA	19.7	76.2	LCST, 483	[27, 29]
PVF	PMMA	19.7	—	LCST, 623	[29]
PPO	copolymer*	3.5	14.0—73.0	LCST, 553-573	[30]
PVC	CPE	—	—	LCST, 393	[31]
CPE (27% Cl)	PMMA	10.8	12.2—72.8	UCST, 330; LCST, 353	[32]
CPE (47.8% Cl)	PMMA	12	12.2—72.8	**	[33]
CPE (36.9-51.6% Cl) Cl)	PMMA	19.8	12.2—72.8	LCST, 373-423	[33]
PE	PIB	2.9	188	LCST, 363	[34]
PMMA	ABS	10	—	LCST, 410	[34]

Notation: PC = polycarbonate, P-ε-CL = poly-ε-caprolactone, PSAN = styrene–acrylonitrile copolymer, PEVA = poly(ethylenevinyl acetate), PVF = poly(vinylidene fluoride), PMA = poly(methyl acrylate), PEA = poly(ethyl acrylate), PMVK = poly(methyl vinyl ketone), PEMA = poly(ethyl methacrylate), PPO = poly(phenylene oxide), and ABS = acrylonitrile–butadiene–styrene copolymer.

*o-Chlorostyrene-*p*-chlorostyrene copolymer.

**"Hour glass".

Analysis of the data obtained by the method of turbidity points in thin films (Table 2) shows that all the phase diagrams have a LCST and that it is as a rule in the region of temperatures traditionally considered as "non-working" temperatures for the corresponding polymer compositions. It is also noteworthy that almost always [with the exception of the polystyrene–poly(methyl vinyl ether) (PS–PMVE) system] no thermodynamic analysis of the phase diagrams and their comparison with known theoretical and experimental data can be found in the literature. For example, the polyisobutylene–polyethylene system (PIB–PE) has a LCST above the liquidus curve according to Tyukova et al.,[34] while according to Flory et al.[6] the system is fully incompatible over the entire range of compositions at temperatures above the melting point T_m. Furthermore, the character of the phase equilibria and the range of critical solution temperatures T_c frequently conflict with the available experimental facts.

As an example, we may quote the PS–PMVE system, since it has been studied most thoroughly: the variation of the LCST with the molecular weight has been demonstrated,[35] a study has been made of the mechanism of the phase separation, and the diffusion coefficient has been found.[24] The values of χ_{12} have been measured at two temperatures; the values obtained suggest a U-shape relation between χ_{12} and T. On this basis, it has been suggested[24] that two critical solution temperatures, namely LCST and UCST, exist in the system. Later two critical solution temperatures T_c were found experimentally for this system:[25] the UCST at 303 K and the LCST at 353 K [sic.]. The intensity of the scattering of a laser beam on passing through the PS–PMVE–benzene system has been measured for constant compositions of the mixture and a variable content of the solvent with subsequent extrapolation to zero content of the solvent.

However, it is noteworthy that extrapolation of the miscibilities of a P–P–S system to the values for the P–P system is impossible not only owing to the error associated with the low concentration limits of the dissolution of high-molecular-weight components in low-molecular-weight solvents but also because of fundamental considerations, since such extrapolation presupposes an additive relation between the miscibilities of the binary and ternary systems, which conflicts with the theories of polymer solutions. Furthermore, additional limitations as regards temperature (apart from the glass points T_g and decomposition temperatures T_{decomp} of the polymers), associated with the crystallisation temperature T_{cryst} and boiling point T_b of the solvent, apply to this method. The identity of the LCST and the T_b of benzene is striking in this connection.[25]

We may note that other investigators[36] showed by the method involving the determination of the velocity of sound and by electron microscopy that the PS–PMVE system, also obtained from solution in toluene, is microheterogeneous when the PMVE content is between 5 and 70% in the range from the normal temperature to 413 K. Evidently these results conflict with the full compatibility of the components, which should obtain in the temperature range investigated in conformity with the phase diagram obtained in previous studies.[23-25] Thus, the final elucidation of the phase equilibrium in this system requires allowance for all the known experimental data.

Such discrepancies throw doubt on the validity of the application of the method of turbidity points particularly when the authors failed to observe reversible turbidity (in the PSAN–PMMA system)[27] or when T_c is very close to T_{decomp} of the components.[29,31-33] The authors of a review[17] draw attention to the necessity to take into account the influence of various chemical processes between the components of mixtures on their compatibility. However, the same investigators failed to attempt in their own study[27] a serious analysis of the system investigated precisely from these standpoints assuming that the weight loss up to 22% in the PVF–PEMA system which they observed does not affect the character of the phase equilibria.

Mixtures with chlorine-containing components, such as PVC and CPE, capable of undergoing dehydrochlorination even at $T = T_g$,[90] which significantly alters the chemical structure and hence also their miscibility with other polymers, merit especial attention from this standpoint. Thus, according to some data,[31] the PVC–CPE (42% Cl) mixtures

are characterised by an equilibrium with a LCST at 393 K, while according to other data[37] these mixtures are compatible to only a limited extent at temperatures below 393 K and the degree of chlorination of CPE must not be less than 48%. For a 30% chlorine content in CPE, the polymer is incompatible with PVC, PMMA, and certain other polymers even on mixing in a common solvent.[38] A phase diagram having both a UCST and a LCST has been published[32] for the CPE (27% Cl)–PMMA system, while an "hour glass" diagram has been obtained for the CPE (47.8% Cl)–PMMA system. In another study[33] the same workers obtained a phase diagram with a LCST for the CPE (49.8% Cl)–PMMA system (Table 2). Such a wide variety of types of phase equilibria within the limits of virtually a single system cannot be explained from a purely thermodynamic point of view if one disregards the chemical reactions occurring during the annealing of the system and also other kinetic factors which include mass-exchange processes and the thermal stability of the polymers. All these factors make the problem of the simultaneous study of phase equilibria and the translational mobility and thermal stability of the components one of the most urgent and general in the study of the compatibility of P–P systems.

Definite advances have been achieved in this field with the aid of a qualitatively different approach to the methodology of the study of P–P systems, namely in the investigation of the local contact regions of polymer components using highly resolving diffusion methods. The principle of these methods is based on the study of the distribution of the concentrations ω in the direction of the diffusion flux x in a local region after diffusional annealing of the specimens in contact over a period t. Such methods include, for example, the method of scanning infrared spectroscopy with a spatial resolution of 100 μm,[39] an interference micromethod with a resolution of ~10 μm,[40] and the electron probe (X-ray spectroscopic) microanalysis whose spatial resolution is ~1 μm.[40–42] There exists a definite correspondence between the form of the concentration profiles and the phase diagrams (Fig.3), which makes it possible to obtain, simultaneously with the diffusion constants, quantitative information about the compositions of the coexisting phases over a wide temperature range.[43] The application of the method of X-ray microanalysis, based on the recording of the characteristic X-ray emission of the element analysed, makes it possible to follow quantitatively, apart from the determination of the above information, the variation of the chemical structure of the components of the systems investigated directly on the basis of the change of the intensity of the analytical line after isothermal annealing.[44]

Various oligomeric and polymer–oligomer systems have now been investigated with the aid of the interference micromethod. Phase diagrams and mutual diffusion coefficients for mixtures have been obtained: elastomers–oligoester acrylates and oligomethylenes,[45,46] PVC–oligoester acrylates,[47] elastomers–epoxy-ologiomers, etc.[48] The influence of the end group, the chain length, and the nature of the components on the phase equilibria and mutual diffusion in mixtures has been studied. The advantages of the local methods, whereby one can determine equilibria which are not established throughout the bulk of the specimen but only at the contact boundary, are particularly evident and it is necessary to investigate more complex P–P systems or rapid processes. Thus in the study of epoxide–rubber hardening systems[49] only the application of the interference micromethod made it possible to follow the evolution of the phase states determined by the varying degree of departure of the system from the critical solution temperatures during the continuous variation of the chemical nature of the epoxide component during the hardening process, to identify the diffusion-controlled stages in the formation of heterogeneous polymer compositions, and to determine the process conditions ensuring a specific regulation of the physicomechanical properties of the material.

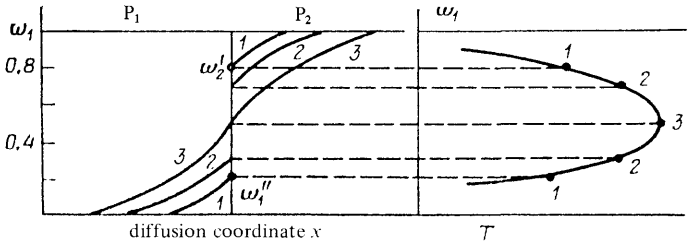


Figure 3. Schematic illustration of the transition from diffusion profiles in terms of ω–x plots to the ω–T phase diagram for the P_1–P_2 system. The numerals opposite the curves (*1* → *3*) correspond to an increase in the annealing temperature (case with a UCST).[43]

The X-ray microanalytical method, whose spatial resolution makes it possible to retain the time scale of the diffusional annealing in the region of minutes, is used in the study of blends of polymers with high molecular weights. This method, the apparatus for which is combined with that for scanning electron microscopy, has been developed in greatest detail and has been used in the study of mutual diffusion and phase equilibria in polymer mixtures with chlorine- and fluorine-containing components, such as PVC–PMMA, PVF–PMMA, CPE–PMMA, PVC–P-ε-CL, etc.[22,44,50–53] The mutual diffusion coefficients and phase diagrams have been obtained for the PVC–PMMA system and the influence of the molecular weight, the chemical stability, and the structure of one of the components as well as the previous history of the system on the phase composition of the mixture has been investigated.[22,44,50,54–56] These experimental data provide the necessary and sufficient information for the consideration of the processes occurring in the system from the instant of the formation of the real mixtures up to the establishment in the latter of the phase structure corresponding in terms of composition to the equilibrium phase diagram, which can be responsible for the discrepancies between the existing experimental results mentioned above. Certain characteristic features of the phase equilibria and of the diffusion and other properties characterising P–P mixtures will be considered below on the basis of the system indicated.

III. PHASE EQUILIBRIA IN THE POLY(VINYL CHLORIDE)–POLY(METHYL METHACRYLATE) SYSTEM

The phase diagrams for mixtures of PVC and PMMA with different molecular weights have been obtained in the temperature range 400–470 K (Fig.4a).[56] The low-temperature branches of the binodals cannot be obtained by this and other methods owing to the loss of translational mobility by the macromolecules in the region of the T_g, while the high-temperature branches (at $T \geq 470$ K) cannot be obtained owing to the intense thermal decomposition of PVC. Fig.4 shows that the regions of the homogeneous mixing expand with increase of temperature, which is characteristic of systems with a UCST; this effect is greater the lower the molecular weight of PMMA.

The critical concentrations (Table 3) of mixtures of PVC and PMMA, corresponding to the mixing of components at the critical points, are close to 0.5 over the entire range of experimental molecular weight ratios M_{PMMA}/M_{PVC}, from 0.45 to 5.12, in contrast to a solution of PVC in the PMMA monomer whose phase diagram is appreciably asymmetric (Fig. 4*b*) and the critical composition corresponds to a comparatively low PVC concentration ($\phi_c = 0.12$). The experimental values of ϕ_c in the PVC–PMMA system, found from the point of intersection of the rectilinear diameter and the composition axes, are compared in Table 3 with the values calculated on the basis of the Flory–Huggins–Scott theory from the equation $\phi_c = n_2^{1/2}/(n_1^{1/2} + n_2^{1/2})$, where n_1 and n_2 are the degrees of polymerisation of the components. Only a qualitative agreement is observed between the experimental and calculated quantities, particularly for molecular weight ratios differing appreciably from unity.

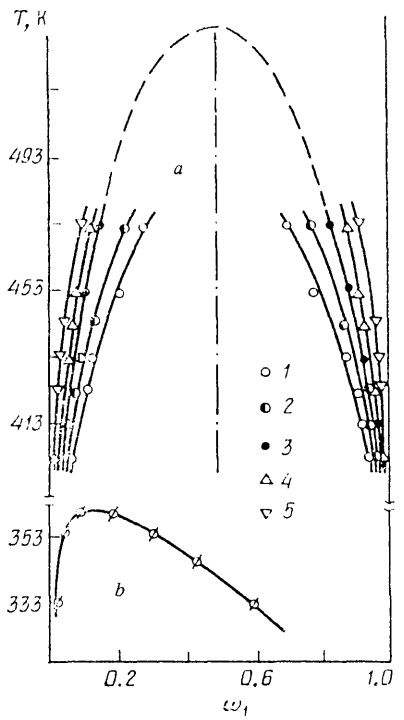


Figure 4. Phase diagrams for the PVC–PMMA (*a*) and PVC–MMA (*b*) systems; $M_{PVC} = 1.4 \times 10^5$; $10^{-5}M_{PMMA}$: 1) 0.64; 2) 1.12; 3) 1.87; 4) 3.02; 5) 7.26.[56]

Table 3. The critical parameters of the PVC–PMMA system.[56–58]

M_{PMMA}/M_{PVC}	φ_c (expt)	φ_c (calc.)	UCST, K
0.45	0.49	0.34	538
0.80	0.50	0.45	522
1.33	0.50	0.51	533
2.15	0.51	0.58	545
5.18	0.51	0.64	556

The influence of the molecular weight on the magnitude and position of T_c has been studied also in the PS–PMVE system.[35] However, it is difficult to reach a conclusion concerning the form of the binodal on the basis of these data, because the temperature range in which they were obtained did not exceed 20 K with the exception of one instance where it amounted to 70 K and it was evident that the binodals are disposed symmetrically; this corresponded to the ratio $M_1/M_2 \approx 1$.

On plotting $\omega_1'(\omega_1'')$–M or $\omega_1'(\omega_1'')$–$1/M$ phase diagrams for isothermal conditions, it is possible to find quantitative relations between the molecular weight and the phase composition of the solution.[45,57] Linear relations have been observed for the PVC–PMMA system: $\omega_1' = \omega_{1,\infty}' + K'M^{-1}$ and $\omega_1'' = \omega_{1,\infty}'' - K''M^{-1}$ (here K' and K'' are empirical constants and $\omega_{1,\infty}'$ and $\omega_{1,\infty}''$ are the solubilities of the components when $M_{PMMA} \to \infty$). Approximate estimates obtained by extrapolating the ω_1'–$1/M$ straight lines to regions of high and low molecular weights showed that an increase of temperature from 433 to 473 K is accompanied by a change of $\omega_{1,\infty}$ from 0.01 to 0.06 in terms of weight fractions of PVC; under these conditions, $(M_{PMMA})_c = 16\,000$ at 433 K, 26 000 at 453 K, and 35 000 at 473 K. Such analysis yields preliminary quantitative information about the miscibility when the molecular weight of one of the components is varied, which is important for the practical employment of the blend.

Theoretical analysis of the experimental binodals is of special interest for the understanding of the processes occurring on blending polymers. Such analysis for the PVC–PMMA system has been carried out within the framework of the classical Flory–Huggins–Scott theory, the improved Flory theory, and the new Flory–Patterson theory.[58] The interaction parameters χ_{12} (Table 4) were calculated from the equation of the binodal based on the Flory–Huggins–Scott theory:

$$\ln \varphi_1' + \left(1 - \frac{n_1}{n_2}\right)\varphi_2' + n_1\chi_{12}(\varphi_2')^2 = \ln \varphi_1'' + \left(1 - \frac{n_1}{n_2}\right)\varphi_2'' + n_1\chi_{12}(\varphi_2'')^2.$$

Table 4. The parameters χ_{12} and $(\chi_{12})_c$ for the PVC–PMMA system as a function of M_{PMMA}.[56,58]

$10^{-5}M_{PMMA}$	$10^3\chi_{12}$				$10^3(\chi_{12})_c$
	413 K	433 K	453 K	473 K	
0.640	2.430	2.280	2.125	2.080	1.640
1.120	1.877	1.714	1.557	1.435	1.130
1.870	1.777	1.520	1.359	1.196	0.824
3.020	1.658	1.381	1.216	1.063	0.645
7.269	1.660	1.274	1.130	0.951	0.434

Account was taken of the experimental values of ϕ_1 and ϕ_2 in the experimental temperature and molecular weight ranges; the $(\chi_{12})_c$ were obtained from the equation

$$(\chi_{12})_c = \frac{1}{2}\left(\frac{1}{n_1^{1/2}} + \frac{1}{n_2^{1/2}}\right)^2 .$$

It is striking that the χ_{12} have low positive values which vary consistently as T and the molecular weight are altered. The relations between the χ_{12} and $1/T$ are linear in the experimental temperature range. Here χ_{12} is almost equal to χ_{21}, which indicates the absence of a concentration dependence of this parameter and is reasonable for the observed symmetry of the binodals. The dependence of χ_{12} on $1/T$

has been used[46,47] for the thermodynamic analysis of P–O blends: the determination of the consolute temperatures, the enthalpy and entropy components of χ_{12}, etc. The linearity of this relation observed for the PVC–PMMA system and the deviation of the constant from the zero value permitted an analogous analysis for the P–P system. The UCST (Table 3), the high-temperature branches of the binodal (see the dashed line in Fig.4*a*), χ_H, and χ_S were determined (Table 5).

Table 5. The values of χ_H and χ_S for the PVC–PMMA system.[56,58]

$10^{-5}M_{PMMA}$	$10^3\chi_H$				10 χ_S	$10^3(\chi_H)_c^*$
	413 K	433 K	453 K	473 K		
0.640	3.35	3.20	3.05	3.00	−1.92	2.56
1.120	3.54	3.41	3.22	3.00	−1.67	2.80
1.872	3.82	3.57	3.39	3.24	−2.05	2.80
4.020	3.90	3.62	3.45	3.40	−2.24	2.89
7.269	4.11	3.72	3.58	3.40	−2.45	2.88

*$(\chi_H)_c = \chi_c - \chi_S$.

Such formal analysis permits the estimation of the contribution of each parameter to the miscibility of the polymers. It follows from Table 5 that χ_H is a decreasing function of temperature, which is the reason for the observed decrease of χ_{12} with increase of T. As the molecular weight rises, χ_H also increases and to a lesser extent at higher temperatures T. At the critical point the quantity $(\chi_H)_c$ is almost constant and independent of the molecular weight except for the system having the lowest molecular weight. Evidently this is associated with the independence of the miscibility parameters δ of the molecular weight in the experimental range of values of M_{PMMA} from 1.12×10^4 to 7.26×10^5. On the other hand, χ_S has negative values, which increase in absolute magnitude with increase of M_{PMMA}.

Comparison of the thermodynamic parameters in Tables 3–5 shows that negative values of χ_S should have a definite significance for P–P systems characterised by a UCST, because they correspond to a positive value of the non-combinatorial entropy ($\Delta S_{non\text{-}comb} > 0$) and make an additional contribution to the free energy of mixing. Their increase with increasing molecular weight probably partly compensates the characteristic decrease of ΔS_{comb} associated with the decreased number of molecules per unit volume. The competition between these two processes apparently explains also the attainment of a plateau on the relation between T_c and the molecular weight as the Θ temperature is approached. The Θ temperature for the PVC–PMMA system, found from the linear plot of $1/T_c$ against $1/M^{1/2}$, is 588 K; it is striking that it lies appreciably above T_{decomp} for the polymers.

Thus it is evident that a high negative value of χ_{12}, ensured by a high non-combinatorial contribution to the entropy of mixing, can obtain in P–P systems with a UCST only at temperatures greatly exceeding those corresponding to their chemical stability. In this connection it is essential to mention the results of Ielenic's study.[20] A negative interaction parameter ($\chi_{12} = -0.0044$) has been obtained for blends of high-molecular-weight PVC and PMMA by the method of neutron scattering. Since the PVC–PMMA system is only partly compatible (Table 1, Fig.4*a*) and is heterogeneous over a wide range of compositions,[13,59] the view, expressed above, that the thermodynamic quantities determined for the specimens using a third component characterise the equilibrium in the P–P–solvent three-component system and cannot serve as criteria of the compatibility of the P–P binary system at a normal temperature is evidently valid. The same order of magnitude (in terms of the absolute value) of the quantity χ_{12} obtained by the neutron scattering method[20] and the values quoted in Table 4 [56,58] suggest that a conformational state of the macromolecules identical with that which should obtain at a temperature above the Θ temperature and corresponding to a non-equilibrium conformation at the experimental temperature is realised on formation of the P–P system in the presence of a solvent.

Thus theoretical analysis of the experimental phase diagram showed that the phase equilibrium in the PVC–PMMA system, characterised by a UCST, depends significantly on the molecular weight of one of the components and that this dependence is qualitatively described satisfactorily within the framework of the Flory–Huggins–Scott theory and the improved Flory theory. However, this agreement obtains only for the ratios $M_1/M_2 \geq 1$ and $M_1 > 10^5$. It has been shown that the deviation of the parameters of the PVC–PMMA system for $M_{PMMA} = 6.4 \times 10^4$ from the theory (see Tables 3 and 5) is associated with the influence of the free volume effect, which is not manifested for higher values of M_1.

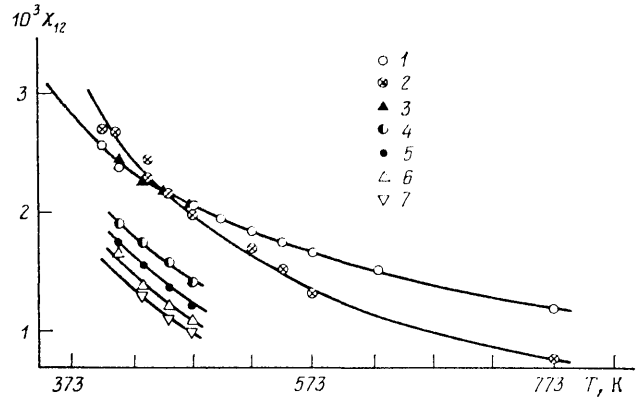


Figure 5. Temperature variation of χ_{12} (1) and the interaction term (2) calculated by Eqn.(1); 3)–7) the values of χ_{12} derived from external binodals as a function of M_{PMMA}.[58] The minima on curves *3*–*7* correspond to curves *1*–*5* in Fig.4.

The influence of these effects has been traced in the analysis of the temperature variations of χ_{12} calculated by Eqn.(1). The contribution of the free volume term B in Eqn. (1) to the overall quantity χ_{12} can be seen from Fig.5, in which the dependence of χ_{12}/Mv_1^* on T (curve *1*), the temperature variation of the interaction term in Eqn.(1) (curve *2*), and the dependence of χ_{12} on T (curves *3*–*7*) are compared. It is seen that curves *4*–*7* are parallel to curve *2*, while curve *3*, corresponding to the system with $M_{PMMA} = 6.4 \times 10^4$, is parallel to curve *1*. Consequently the miscibility of PVC and PMMA for $M_{PMMA} > 6.4 \times 10^4$ is determined solely by the interaction of the components, while under conditions where $M \leq 6.4 \times 10^4$ the difference between the free volumes exerts an appreciable influence. Evidently the latter influence will increase with decrease of M_{PMMA} and with increase of the difference between M_{PVC} and M_{PMMA}. However, calculations showed[58] that the appearance of a

LCST above the UCST in this system (U-shaped dependence of χ_{12} on T) requires necessarily the complete conversion of one of the polymers into the monomer, which would ensure an increase of τ by an order of magnitude and the predominance of the contribution by the second term of Eqn.(1) to the overall quantity $\chi_{12}/M_1 v_1^*$. Analogous calculations have been carried out for the PS–PMMA system and it has been shown that the UCST lies above the decomposition temperatures of the polymers.[60]

Although analysis of this kind is qualitative and in no way replaces the experimental study of compatibility, its employment makes it possible to account for certain features of the phase equilibria in specific systems.

Many attempts have been made recently[15,61–64] to determine the compatibility of polymers (including PVC) with stereoregular components. Fig.6[58] presents sections of the binodal for the PVC–*iso*-PMMA system; it is seen that PVC and stereoregular PMMA (as well as α-PMMA) are partly compatible and phase equilibrium is characterised by the presence of a UCST; secondary processes (associated with crystallisation or other structural transformations) are superimposed on the amorphous equilibrium and complicate its character and the form of the binodal above the melting point of *iso*-PMMA. At temperatures below the melting point, *iso*-PMMA is less compatible with PVC than *a*-PMMA, while above it the solubility of *iso*-PMMA in PVC increases appreciably. The overall tendency in the phase equilibrium and the PVC–*iso*-PMMA system, determined by sections of the binodal,[58] does not conflict overall with the data of other workers, demonstrating a particular degree of limited compatibility of the system in the range $T < T_m$ (melting point), T_{fl} (fluidity temperature) of the polymers.[15,62,64]

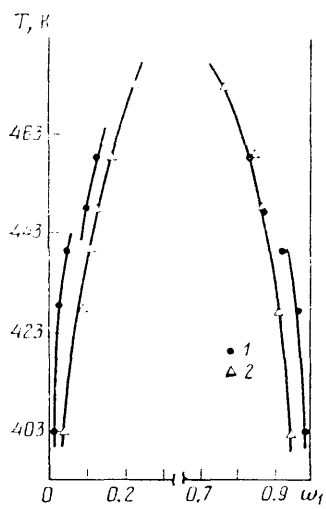


Figure 6. Temperature variation of the compositions of the coexisting phases in the PVC–*iso*-PMMA (1) and PVC–*a*-PMMA (2) systems with identical molecular weights.[58]

IV. MUTUAL DIFFUSION OF POLY(VINYL CHLORIDE) AND POLY(METHYL METHACRYLATE)

The study of the diffusion coefficients and of the characteristics of their variation is a necessary component in the investigation of P–P mixtures, because, together with phase diagrams, they constitute the theoretical basis for the determination of the conditions for the processing of blends, the formation of the phase structure of the material, and the estimation of its thermodynamic and kinetic stabilities.

The mutual diffusion coefficients D_v for PVC and PMMA, determined in the temperature range between T_g and T_{decomp} by X-ray microanalysis, vary in the range from 10^{-14} to 10^{-17} m^2 s^{-1}.[54] Table 6 presents the values of D_v measured at 453 K and the activation energies for diffusion E_D, calculated from the temperature relations $D_v(T)$. The energies E_D for blends with *a*-PMMA are independent of the molecular weight of the diffusing species and the diffusion medium and amount on average to 113 kJ mol^{-1} for the diffusion of PVC in PMMA (D_{12}) and to 134 kJ mol^{-1} for the diffusion of PMMA in PVC (D_{21}). These values are close to the activation energies for viscous flow E_η of the components and demonstrate the segmental character of the movement of macromolecules in polymer blends.

Table 6. Diffusion coefficients and activation energies for diffusion in the PVC–PMMA system.[54]

Diffusing species (*M*)	Diffusion medium	$10^{15}D_v$, m^{2}s^{-1} (453 K)	E_D, kJ mol^{-1}
PMMA (64 000)	PVC C-70 (140 000)	3.90	137
PMMA (112 000)	ditto	1.40	131
PMMA (187 200)	»	0.50	136
PMMA (302 400)	»	0.21	136
PMMA (726 900)	»	0.09	134
iso-PMMA (100 000)	»	0.43	—
PVC C-70 (140 000)	PMMA (64 000)	2.50	115
Ditto	PMMA (112 000)	1.50	112
»	PMMA (187 200)	1.20	112
»	PMMA (302 400)	1.10	115
»	PMMA (726 900)	1.00	115
»	*iso*-PMMA (100 000)	0.35	—

The diffusion parameters presented in Table 6 are fairly unique not only because they have determined for the first time for the PVC–PMMA system but also because nowadays the diffusion parameters of macromolecules in a medium consisting of similar macromolecules are known only for a small number of systems. Thus the self-diffusion and mutual diffusion coefficients have been determined by the radioactive label and spin-echo relaxation methods for polymers and systems: PS, styrene–n-butyl acrylate copolymer (in Bueche's work), PS_1–PS_2,[65] natural rubber (NR), synthetic isoprene rubber (SIR)–NR system,[66] polydimethylsiloxane (PDMS),[67,68] and certain others.[69–72] Certain systems in the elastic and fused states have been investigated by local methods, particularly by the interference micromethod: PIB–synthetic buta-1,4-diene rubber (SBR), PE–atactic polypropylene (*a*-PP), PE–SIR, etc.[73,74]

Analysis of the available data showed that the values of D determined by various workers at temperature above T_{fl} and T_m are 10^{-12}–10^{-14} m^2 s^{-1}, while in the highly elastic state they are lower by 3–5 orders of magnitude (10^{-15}–10^{-19} m^2 s^{-1}). The values of D_{12} and D_{21} obtained for the first time with the aid of local X-ray microanalysis agree well with the values of D determined by the traditional methods. Fig.7 illustrates the temperature variation of the coefficients D_{12} and D_{21} for the PVC–PMMA system and those of D^* and D_{12}^* for other systems in terms of the reduced variables lg D and $T-T_g$.

It is seen that the values of D for various polymers with similar molecular weights fit on a single straight line to within 40%. It is reasonable that the values of D_{12}^* for the diffusion of SIR in vulcanised natural rubber, D_{12}^* for the methylvinylpyridine synthetic rubber (SMVPR), containing a polar component in the side chain, as well as D_V for the PVC–*iso*-PMMA system are exceptions. Evidently the mechanism of the diffusion process in the PVC–PMMA system is analogous to the mechanism of the diffusion of other linear amorphous polymers: PS, NR, poly(butyl acrylate) (PBA), etc. The values of D for a further series of polymers, such as polyacrylates, polymethacrylates, α-PP, and amorphous rubbers, will probably fit on the straight lines in Fig. 7. Deviations are to be expected for systems with specific properties (polar, crystallisable, and structured systems).

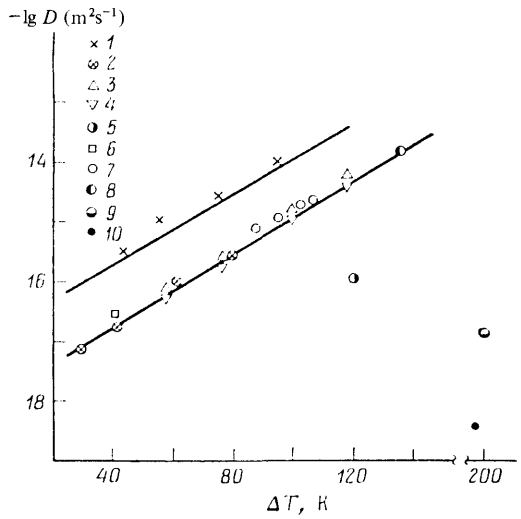


Figure 7. Dependence of the diffusion coefficient D on the difference between the experimental temperature and T_g: 1) D_{21} for PVC–PMMA ($M = 6.4 \times 10^4$); 2) D_{21} for PVC–PMMA ($M = 7.26 \times 10^5$); 3) D_{12} for PVC–PMMA ($M = 6.4 \times 10^4$); 4) D_{12} for PVC–PMMA ($M = 7.26 \times 10^5$); 5) D_{21} for PVC–*iso*-PMMA ($M = 10^5$); 6) D^* = SBR;[69] 7) D^* for PBA; 8) D_{12}^* for PS; 9) D_{12}^* for SIR–NR_{vulc};[66] 10) D_{12}^* for SMVPR.[70]

The studies of the dependence of D on the molecular weight of the diffusing species and the diffusion medium have acquired much importance for the understanding of the mechanism of the translational movement of macromolecules in P–P systems. The influence of the molecular weight of the diffusing species for a constant molecular weight of the medium on the diffusion of PMMA in PVC (D_{21}) and the influence of the varying molecular weight of the diffusion medium for a constant molecular weight of the diffusing species on the diffusion of PVC in PMMA (D_{12}) are illustrated in Fig. 8. It is seen that, with increase of the molecular weight of the diffusing species, the absolute values of D diminish. In the experimental molecular weight range and for all the experimental temperatures, the following relation holds:

$$D = AM^{-b}, \qquad (3)$$

where A and b are empirical coefficients. The coefficient b is a function of temperature and decreases with increase of temperature from 1.57 at 413 K to 1.40 at 473 K.[54]

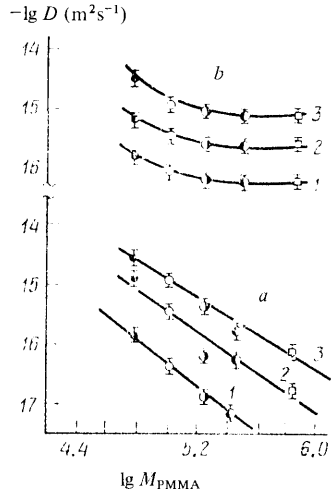


Figure 8. Dependence on the diffusion coefficients D_{21} (a) and D_{12} (b) on M_{PMMA} at different temperatures (K): 1) 413; 2) 433; 3) 453.[54]

A change in the molecular weight of the diffusion medium for a constant molecular weight of the diffusing species leads to the dependence of $\lg D$ on $\lg M$ characteristic for binary systems; the plot has the form of a concave curve described by the expression $\lg D_{12} = \lg D_{12}^{\infty} + n/M_2$, where $n = 3.5 \times 10^4$ is a constant and D_{12}^{∞} is the diffusion coefficient at $M \to \infty$. It is striking that D_{12}^{∞} is attained for the ratio $M_{diff.species}/M_{medium} = 1$ and is not related to M_c (the molecular weight between the entanglement nodes).[54]

The available theories of macromolecular movement are based on the concept of a randomly intertwined structure of the amorphous polymer with a characteristic value of M_c. Bueche's theory considers the energy lost in friction betwen sections of the chain in the course of the translational movement of the molecule and takes into account the entanglements which retard the movement, because one molecule carries behind it others intertwined with it. The theory predicts a dependence of D on M raised to the power 3.4. The "reptation" models of de Gennes[75,76] and Edwards,[77,78] which also take into account the entanglement nodes but deal with the movement of macromolecules which, in essence, bypass these nodes during movement in a closed "tube", significantly differ from Bueche's model. According to De Gennes and Edwards,[75–78] the power exponent b in Eqn. (3) should be 2.

We may note that the values of b determined for the PVC–PMMA system are significantly lower than those predicted theoretically, although the molecular weights of the components of the diffusion pair exceed the molecular weight corresponding to the formation of an entanglement network [M_c(PMMA) = 3×10^4] and are not constant, as predicted by the theory.

The fact that the entanglement network does not influence the diffusion of the macromolecules was noted in an earlier study[66] of D_{12}^* in the SIR–NR system; it was later noted by Tanner[67] and was subsequently formulated in a general

form[79] in the analysis of the experimental data. However, the controversy on this question still continues.[72,76,80,81] It is therefore of interest to analyse the available experimental data for the $D = f(M)$ relations. The studies of the self-diffusion of normal paraffins and PE oligomers yielded $b = 1.7$. According to Bresler et al.,[66] D_{12}^* is proportional to the molecular weight raised to the power of −1.3. The self-diffusion of PEO and PDMS has been investigated[67,68] over a wide range of molecular weights and the power exponent b proved to be 1.7. When the partial self-diffusion coefficients were investigated, it was found that $b = 1$. Kumagai et al.[65] investigated D^* and D_{12}^* for PS; they obtained $b = 1$ for $D_{12}^*(M)$ and $b = 2$ (2.7) for $D^*(M)$. It was also possible to calculate b from Skewis's data[69] (D_{SBR}^*) and the data of Nikiforova et al.[74] ($D_{vPP-SIR}$); $b = 1.65$ and 1.2–1.4 in the former and latter cases respectively.

Thus the experimental values of b can be divided into two groups—those determined from the self-diffusion coefficients D^* and those found from the partial self-diffusion and mutual diffusion coefficients D_{12}^* and D_v (Table 7). Since the values of D_v in infinitely dilute solutions characterise the translational mobility of the polymer in another polymer, it follows that D_v and D_{12}^* have a similar physical significance. For the first group, the parameters b vary from 1.7 to 2, which agrees fairly well with the values predicted theoretically.[76] However, for the second group, b has values ranging from 1 to ~1.6. Evidently the modern theory does not as yet yield a description of the translational movement of macromolecules in P–P systems characterised by the coefficients D_v and D_{12}^* and corresponding to the experimental results. Isolated attempts have only been made to account for such experimental observations by a mixed mechanism of the macromolecular movement.[81]

Table 7. The parameter b in Eqn.(3) for different P–P systems.[45,54,66–71,74].

System	D	b	System	D	b
SIR-NR	D_{12}^*	1.31	PE*	D^*	1.7
PS-PS	D_{12}^*	1.0	PS	D^*	2 (2.7)
PDMS-PDMS	D_{12}^*	1.0	PDMS	D^*	1.7
PP-SIR	D_v	1.2–1.4	SBR	D^*	1.65
PE-SIR	D_v	1.2			
PVC-PMMA	D_v	1.4–1.57			

*Oligomers.

Thus the experimental studies of blends of PVC and PMMA and analysis of data for other systems have shown that the thermal translational mobility of macromolecules in P–P systems is determined, in the case of amorphous linear components, by diffusion coefficients in the range ~10^{-15}–10^{-19} $m^2\ s^{-1}$ at temperatures above T_g and in the range 10^{-12}–10^{-14} $m^2\ s^{-1}$ above T_{fl} (or T_m in the case of crystallisable polymers); this mobility depends on the molecular weight of the diffusing species in accordance with Eqn.(3) and $b < 2$ and is independent of the molecular weight of the medium when $M_{diff.sp.}/M_{medium} \leq 1$. Attention should be drawn to the fact that the translational mobility of the macromolecules in the P–P system is on the whole low on the macroscopic time scale and yet is fairly high on the microscale, particularly at temperatures above T_g, i.e. at the processing temperature and at the real temperatures at which many P–P systems are actually used. This must be taken into account in considering certain features of the formation of the phase structures of polymer blends.

V. THE PHASE STRUCTURE OF HETEROGENEOUS BLENDS OF POLY(VINYL CHLORIDE) AND POLY(METHYL METHACRYLATE)

Blends based on PVC and PMMA, formed from the melt and the solution and in other ways, are heterogeneous systems with a large area of the interface in the range from room temperature to the decomposition temperatures of the components.[12,13,59,82] This agrees well with the limited miscibility of the polymers, which follows from the phase diagrams (Fig. 4*a*). However, the results of indirect measurements of the comptability of PVC and PMMA (Table 1) indicate discrepancies between the absolute compositions of the coexiting phases obtained by different workers.

In this connection it must be emphasised that the low translational mobility of the macromolecules and the high viscosity of P–P systems, which prevent their separation into phases during the finite period of the experiment and which lead to the formation of kinetically stable metastable disperse structures,[83] at the same time are responsible also for the capacity of P–P systems for supercooling. The latter factor should result in the variation of the composition of the coexisting phases as a function of temperature, time, the quality and concentration of the solvent, and other specific processing conditions. The specific features of the translational mobility on the macroscale and the microscale are such that the range of variation of the composition can extend over a large temperature and concentration range: according to the data in Table 1 and the paper of Walsh and McKeown,[84] the composition varies within the limits from incompatibility to complete miscibility. The question arises whether most of the information available today on the compatibility of various P–P systems,[16] including the PVC–PMMA system (Table 1), does not in fact refer to real materials obtained under specific processing conditions and not to equilibrium P–P systems. Examination of this question appears to be extremely important for the understanding of the entire problem of phase equilibria in polymer–polymer systems—from the critical assessment of the methods for the determination of phase diagrams and the type of phase equilibria in P–P systems to the stability of composite materials.

The influence of the conditions in the preparation of blends of PVC and PMMA on the limits of their miscibility has been investigated[13,59] by electron microscopy (Table 1). It has been shown that the character of the disperse structure and also the limits of its manifestation depend on the concentration and rate of evaporation of the solvent; the influence of the quality of the solvent on the miscibility is illustrated in Fig. 2.[22]

The present level of development of analytical electron microscopy combined with methods for the calculation of the dimensions of the disperse phases and X-ray microanalysis for the identification of the phase composition, on the one hand, and also the familiar theories of mass transfer in disperse systems, on the other, make it possible nowadays to proceed tc the analysis of the disperse phase structure of P–P blends from the standpoint of the kinetics of the attainment of phase equilibria.

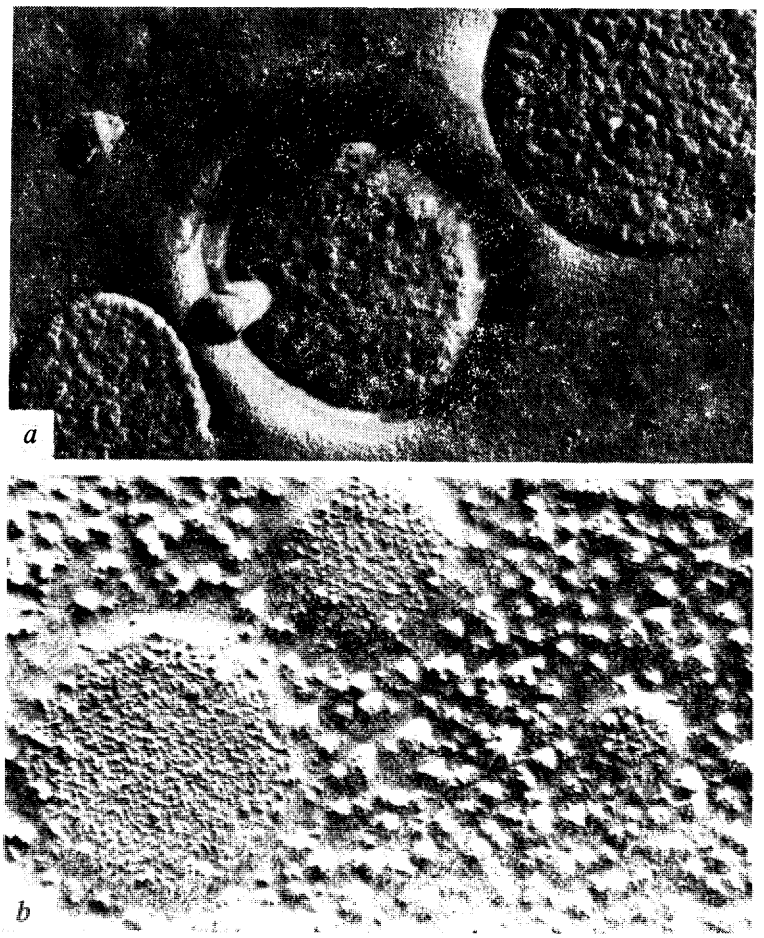


Figure 9. Photomicrographs of the PVC–PMMA system (1 : 3) obtained from solution in cyclohexanone: *a*) before annealing; *b*) after annealing for 30 min at 433 K.[82]

Thus a special study has been made[82] of the influence of the conditions of preparation and thermal annealing on the phase structure of PVC–PMMA blends in comparison with the phase diagrams obtained by Chalykh and Sapozhnikova.[56] The blends prepared from solutions in cyclohexane or THF are initially in a state far from phase equilibrium. X-Ray microanalysis has shown that the compositions of the dispersion medium (PMMA) and the disperse phase (PVC) are supersaturated relative to the corresponding solubility curve on the diagram in Fig. 4*a*. The higher the rate of evaporation of the solvent and the lower the film formation temperature, the greater the deviations from the phase diagram. Thermal annealing of such specimens at a temperature higher by 30 to 40 K than T_g for the components leads to additional phase separation (Fig. 9). The composition of the disperse phases then tends to that of the coexisting phases which follows from the phase diagram at the given temperature. It is striking that an increase of the duration of annealing does not alter the composition of the coexisting phases but does affect the character of the distribution of species with respect to size. A decrease of the concentration of the finely disperse phase and an increase of the size and number of large particles in the PVC–PMMA system take place in conformity with the redistribution of the substance in the direction from the surfaces of the small particles towards the large particles observed for low-molecular-weight systems. The kinetics of this process are described by the Lifshits–Slezov theory, according to which the change in the number of species during prolonged annealing is defined by the equation

$$\partial N/\partial t = (2\sigma D c_p V_m/r^*)\,(RT\partial/\partial r\,[(r-r^*)N(r,\ t)/r^2]), \qquad (4)$$

where σ is the interfacial tension, D the diffusion coefficient, c_p the solubility at $r \to \infty$, V_m the molar volume, r the radius of the particle, and r^* the equilibrium radius of species in the dispersion medium.

The solution of this differential equation for the Gaussian distribution of particles with respect to dimensions is given by the equation

$$N(0)/N(t) = 1 + t/\tau \qquad (5)$$

where

$$\tau = 9RT/8D\sigma V_m^2 c_p r^3(0)\,. \qquad (6)$$

The applicability of the Lifshits–Slezov theory to P–P systems has also been demonstrated to another study[85] in relation to the polybutadiene ($M = 1.5 \times 10^4$)–poly(propylene oxide) ($M = 1.5 \times 10^3$) system. On the basis of electron microscopic

observations on the kinetics of the transformation of the disperse phase structure and on the basis of Eqns.(4)–(6), the phase diagram has been obtained for this system, characterised by a UCST.

Thus it is evident that, by following the kinetics of the changes in the phase structures of polymer blends, it is possible to determine the miscibility of the components; and, conversely, knowing the miscibility and diffusion parameters, it is possible to predict with the aid of Eqn.(4)–(6) the changes which will occur in the disperse system during use.

Fig.10 presents the phase diagram for the PVC–PMMA system and illustrates the position of the spinodal calculated on the basis of the Flory–Huggins–Scott theory from the equation

$$(\chi_{12})_{sp} = \frac{1}{2}\left[\frac{1}{n_1(\varphi_1)_{sp}} + \frac{1}{n_2(\varphi_2)_{sp}}\right].$$

Lines corresponding (according to different authors' data) to the limits of the miscibility in the system, obtained at normal temperatures but using a solvent, are drawn on the diagram parallel to the ordinate axis. Comparison of the positions of these straight lines relative to the binodal and the spinodal in different temperature ranges demonstrates the changes which should occur in the specimens during thermal annealing and also the causes of the quantitative discrepancies between the results of different workers.

It can be seen that, with the aid of solvents, disperse systems corresponding to a metastable state are formed (shaded region between the binodal and the spinodal) over a wide temperature range. This is naturally the reason why the annealing of such systems at temperature above T_g alters the compositions of the coexisting phases in the direction determined by their positions relative to the binodal. Thus the system obtained from a solution in cyclohexanone (straight line 4 in Fig.10) was initially supersaturated relative to the equilibrium compositions of the coexisting phases, which was demonstrated by X-ray microanalysis and electron microscopy. Annealing of such a system at 433–443 K leads to a thermally induced phase separation (Fig.9) and to a decrease of the miscibility limits ω_1'' and ω_2'), while at 473 K it leads to their increase and the dissipation of the particles of the disperse phase.[82] The displacement of ω_1'' and ω_2' along the composition line during annealing is indicated in Fig.10 by arrows.

An analogous displacement of the composition points on the phase diagram has been observed during the annealing of a system prepared from solutions in THF, DCE, and benzene or from the melt after rapid cooling.[22,50,56,82] It is noteworthy that the observed nucleation decomposition and growth of the particles of the disperse phase confirm that the system formed initially was located in the metastable region of the phase diagram.

Thus the phase diagram determines the general trend in the variation of the disperse phase structure of the blend during thermal annealing. Thermally induced phase separation is not then always a sign of a LCST; it can be also a consequence of kinetic processes involving the establishment in the system of the equilibrium compositions of the coexisting phases. It is striking that in this case irreversible changes take place in the phase structure of the polymeric material obtained initially.

At the present time the kinetics of the phase separation of P–P systems via both spinodal and nucleation mechanism have been investigated very little indeed. It follows from a review[86] or another communication[87] that the efforts of investigators have been directed towards the search for and elucidation of the conditions for the spinodal or nucleation mechanisms of the decomposition of P–P systems. However, the question arising from the study of the kinetics of the attainment of phase equilibria in the experimental determination of binodal and spinodal curves remains open. The large number of unexplained contradictory data on the compatibility of polymers, so frequently discussed in the literature[15,16,59,94] (and other communications), is probably in fact associated with this factor.

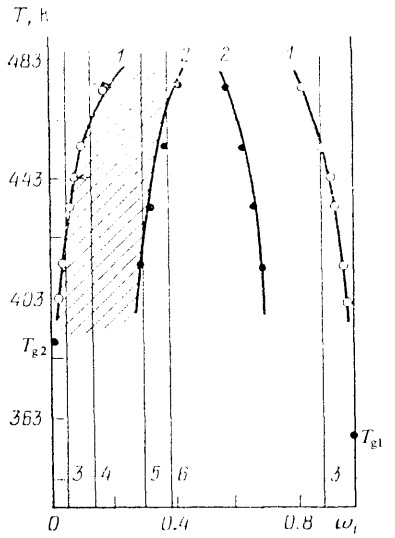


Figure 10. Phase diagram for the PVC–PMMA system: 1) sections of the binodal; 2) sections of the spinodal. The vertical lines correspond to the limits of compatibility of the system obtained using a solvent according to different data: 3) Razinskaya et al.;[13] 4) Matveev et al.;[82] 5) Tager et al.;[14] 6) Shrer et al.[15]

VI. THE INFLUENCE OF IRREVERSIBLE THERMAL DEGRADATION PROCESSES INVOLVING THE CHLORINE-CONTAINING COMPONENTS ON THE MISCIBILITY IN POLYMER BLENDS

The kinetic thermal decomposition processes influencing irreversibly the compatibility of polymers have been examined for at least two reasons. The first is associated with the stability of the phase structure of the blends during their preparation and use and the second with the very problem of the construction of phase diagrams, because the low thermal stability combined with the high viscosity of the polymers actually creates the problem of the attainment of equilibrium under the conditions of isothermal annealing without appreciable chemical transformations. This applies particularly to blends whose composition includes chlorine-containing components (PVC, CPE, etc.), which are capable of intense dehydrochlorination even at $T > T_g$. Numerous data, to a large extent contradictory (see Section II), have now been obtained on the compatibility of polymers with participation of PVC and CPE,[31–33,37,38], but special studies of the influence of their thermal decomposition on compatibility with other polymers have not been made. The application of local X-ray microanalysis made it possible to obtain simultaneously information about the phase diagrams, the diffusion constants, and the thermal stability parameters of chlorine-containing components, which made it possible to demonstrate

quantitatively the influence of thermal decomposition on the character of the phase diagrams of the PVC–PMMA and CPE–PMMA systems.[44,48]

The kinetic curves for the thermal decomposition of PVC at early stages are presented in Fig. 11*a*. The range of times investigated was chosen in accordance with those necessary to obtain equilibrium values of ω_1'' and ω_2'. These data on the kinetics of the decomposition of PVC, obtained with the aid of X-ray microanalysis, are consistent with the familiar data of different workers.[89–91]

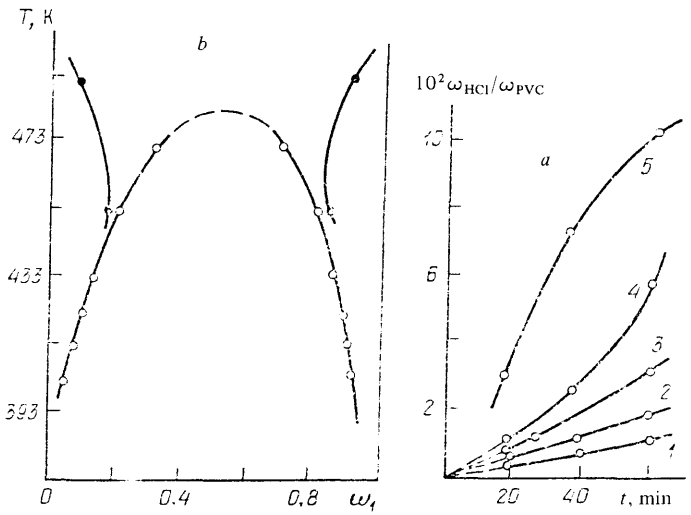


Figure 11. *a*) Kinetic curves for the dehydrochlorination of PVC at different temperatures [*T* (K): 1) 433; 2) 443; 3) 453; 4) 473; 5) 493]; *b*) variation of the phase structure of the PVC–PMMA system after annealing under the conditions of intense thermal decomposition (filled circles).[88]

Fig. 11 shows that annealing at 423–433 K for 60 min and at 443–453 K for 30 min leads to a loss of chlorine equivalent to a weight fraction of only 0.01. Such a change in the chemical structure does not influence the overall form of the binodal characteristic of systems with a UCST. In this case, when the temperature or duration of the annealing exceed the temperature of the chemical decomposition or the induction period of the decomposition reaction (for example, the system has been annealed at 493 K for 20 min or at 453 K for 60 min), the miscibility of the polymers diminishes. The values of ω_1'' and ω_2' obtained under these conditions impart to the phase diagram the "hour glass" character (Fig. 11*b*). However, such a change in the temperature variation of ω_1'' and ω_2' should be explained by the decrease of the miscibility of the components on formation of unsaturated conjugated bonds and partial structure formation in PVC [89] and not by the thermodynamic characteristics, as has been done in a number of studies[32,33,92,94] on blends with chlorine-containing components. Vigorous thermodynamic decomposition processes occurring for certain values of *T* and *t*, limited the possibility of obtaining the complete binodal for the PVC–PMMA system in two investigations.[42,56]

Whereas the PVC dehydrochlorination processes have been studied in fair detail and the variation of the compositions of the coexisting phases illustrated in Fig. 11*b* may prove to be self-evident, in the case of other chlorine-containing polymers, in particular CPE, the relation between the phase equilibrium and the thermal decomposition is significantly more complex.

The miscibility curves for the CPE (62% Cl)–PMMA system and the kinetic CPE thermal degradation curves are illustrated in Fig. 12.[44,88] The phase diagram is complex and resembles the type of diagrams with a "latent maximum", familiar in metallography, which is characteristic of systems undergoing chemical transformations during thermal annealing.

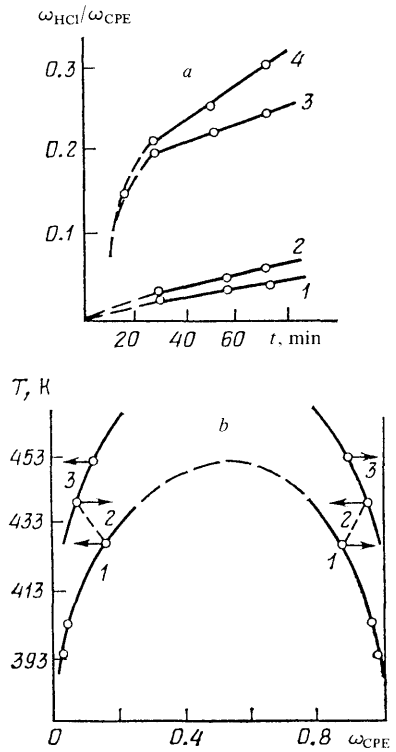


Figure 12. *a*) Kinetic curves for the dehydrochlorination of CPE at different temperatures [*T* (K): 1) 403; 2) 428; 3) 439; 4) 458]; *b*) "composition–temperature" curves for the CPE–PMMA system (for explanation, see text).[95]

We shall consider the dehydrochlorination process occurring during the annealing of the system. It follows from the kinetic curves (Fig. 12*a*) that up to 428 K dehydrochlorination proceeds at a constant rate up to an annealing time of 80 min and the loss of HCl from the CPE specimen amounts to a weight fraction not exceeding 0.03. At 439 K a sharp increase of the rate of elimination of HCl is observed already for short thermal exposures and the loss of HCl is in this case equivalent to a weight fraction of 0.23. An increase of temperature to 453 K hardly alters the degree of dehydrochlorination compared with 439 K. Thus initially a sharp increase of the rate of evolution of HCl is observed (at temperatures above 428 K) and this is followed by retardation, probably owing to the decreased overall chlorine content in the specimens and the appearance of CPE having a higher stability.[93]

We shall now examine Fig.12*b* and compare it with Fig.12*a*. Sections *1* on the "composition–temperature" curve indicate an increase of the miscibility of CPE and PMMA with increase of temperature to 428 K. The chlorine content in CPE is in this case 61%. The jump along sections *2* at 439 K corresponds to a change in the chlorine content in CPE up to 39% (sections *2* are designated in Fig.12*b* by dashed lines because the process is reversible). An increase of temperature to 453 K for an annealing time of 25 min does not alter the chlorine content in the specimen and the values of ω_1'' and ω_2' increase (section *3*). It is seen from the above comparison that this system represents a combination of two systems: CPE (61% Cl)–PMMA and CPE (39% Cl)–PMMA. Like the PVC–PMMA system, the two systems are characterised by phase diagrams with a UCST, but the CPE containing 39% Cl is less compatible with PMMA than the CPE containing 61% Cl. This fact can be satisfactorily accounted for by the extremum in the variation of $(\delta_1-\delta_2)^2$, where δ_1 and δ_2 are the miscibility parameters of PMMA and the CPE decomposition products respectively, with the chlorine content in CPE (Fig.13).

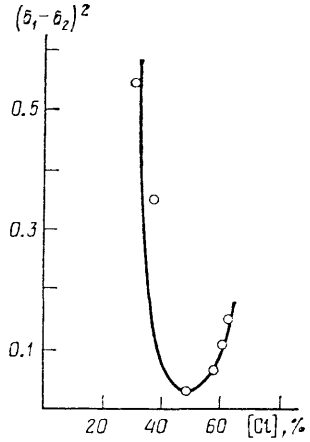


Figure 13. Dependence of $(\delta_1-\delta_2)^2$ on the chlorine content in CPE for the CPE–PMMA system; the values of δ were calculated from the additive contributions by different atomic groups.[95]

Thus it has been shown that the stability of chlorine-containing polymers and their decomposition kinetics have a decisive influence on their compatibility with other polymers and on the character of the phase diagrams for the blends. The extremum in the variation of the miscibility with the chlorine content in the specimen suggests that both trends in the variation of the miscibility operate—both towards its decrease and towards its increase as a function of the thermal decomposition conditions. Thus the slower decomposition of CPE, which depends on the initial PE, the conditions and degree of chlorination, etc., shifts the positions of ω_1'' and ω_2' along section *2* in Fig.13 towards higher values, while longer annealing (for $t > 25$ min), which leads to structure formation in CPE, entails a decrease of ω_1'' and ω_2'. The possible movements of the composition points are indicated by arrows in Fig.13. The combination of the characteristic features of the kinetics of the thermal decomposition of CPE with the complex dependence of the miscibility on the chlorine content in the polymer have in fact enabled the authors[32,33] to obtain a wide variety of types of "phase equilibria" within the limits of the single CPE–PMMA system; diagrams I, III, and V (Fig.1). The results of Chalykh and co-workers[44,88] have shown that the complete description of systems containing unstable components requires a more complex model taking into account the time variation of not only the temperature and composition but also of the chemical structure of the system.

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Thus the review has considered many specific phenomena and properties characteristic of P–P systems and determined mainly by the non-equilibrium nature of their phase structure. The non-equilibrium structure, associated with the low translational mobility and thermal stability of the polymers, arises under the real conditions for the formation of the blends and is manifested by a deviation of the compositions of the disperse phase and the dispersion medium from the equilibrium compositions of the coexisting phases. It reflects the previous history of the blends and influences the mode of variation of the properties during further use. This is observed in experimental studies of the miscibility of polymers and constitutes the basis of numerous contradictions in results obtained by different workers. The data on the translational mobilities of the components of polymer blends examined in this review show that, the attainment of real advances in the study of the equilibrium states in condensed P–P systems requires the abandonment of the traditional integrated methods in favour of local methods employed at a microlevel. In this connection it appears useful to develop and apply the methods of analytical electron microscopy in the study of P–P systems. Highly resolving analytical methods make it possible to carry out a combined study of the phase equilibria, translational mobilities, and thermal decomposition processes, which is essential both from the standpoint of the reliability of the phase diagrams and for their practical employment.

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Institute of Physical Chemistry,
USSR Academy of Sciences,
Moscow

Translated from *Uspekhi Khimii*, 53, 1852-1890 (1984) U.D.C. 577.15.02

General Characteristics of the Changes in the Thermal Stability of Proteins and Enzymes After the Chemical Modification of Their Functional Groups

G.D.Kutuzova, N.N.Ugarova, and I.V.Berezin

The principal structural and physicochemical factors determining the stability of protein macromolecules in solution and the characteristics of the structure of the proteins from thermophilic microorganisms are examined. The mechanism of the changes in the thermal stability of proteins and enzymes after the chemical modification of their functional side groups and the experimental data concerning the influence of chemical modification on the thermal stability of proteins are analysed. The dependence of the stabilisation effect and of the changes in the structure of protein macromolecules on the degree of modification and on the nature of the modified groups and the groups introduced into proteins in the course of modification (their charge and hydrophobic properties) is demonstrated.
The great practical value of the method of chemical modification for the preparation of stabilised forms of biocatalysts is shown in relation to specific examples.
The bibliography includes 178 references.

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I. INTRODUCTION

The problem of the stability of globular proteins (and enzymes), i.e. the problem of the determination of the relation between the structure and stability of biomacromolecules, has been and remains one of the most important and complex problems of the modern physical chemistry of biopolymers which have still not been solved. The problem of increasing the stability of enzymes in relation to various denaturing influences is closely related to the first problem as regards practical needs, because, without knowing the fundamental structural factors determining the stability of the protein globule, it is impossible to alter it in a specific manner. The importance and the necessity for the solution of these problems arose as a consequence of the development of modern biotechnology, which involves the carrying out of many enzymic processes under extreme conditions (in particular, at elevated temperatures).

Numerous data show that there is apparently no single general principle governing the formation of a stable protein conformation and hence there is no single universal method for the stabilisation of proteins. The correlations established in recent years between the primary structure and stability of biomacromolecules are valid only for a limited number of proteins within a specific class.[1] Comparison of the primary, secondary, and tertiary structures of enzymes isolated from thermophilic sources and distinguished by a higher stability with their labile analogues reveals a wide variety of structural characteristics of thermophilic proteins and enzymes responsible for their increased stability as well as a few common features. Nevertheless the knowledge of the main structural factors determining the stability of the native conformation of the protein in solution makes it possible to formulate the fundamental principles of its stabilisation.

One of the most widely used methods for the alteration of the properties (in particular, their stability) of proteins and enzymes in solution is the chemical modification of their functional groups not involved in the active centre. The chemical modification is frequently the first stage of the procedure for obtaining stabilised insoluble enzyme preparations. In many cases the change in the stability of the enzyme as a result of covalent immobilisation is caused not only and not so much by its binding (covalent and non-covalent) to the carrier as by the chemical modification of its functional groups. Chemically modified stabilised soluble enzymes have a number of advantages over insoluble enzymes, in particular, they exhibit a high catalytic activity and have a weaker antigenic activity, which is important for medical applications.

The stabilisation of enzymes in nature is achieved as a result of mutations, i.e. the replacement of a small number of some aminoacid residues by "suitable" other aminoacid residues both within and on the surface of the protein globule. Such stabilisation is apparently a consequence of "natural selection" occurring as a result of changes in the conditions of the existence of the given class of microorganisms (for example, following an increase of temperature), whereupon among the multiplicity of isoenzymes modified by mutations, only those which exhibit a sufficiently stable conformation under extreme conditions "survive". On the other hand, the artificial stabilisation of enzymes by chemical modification can be achieved only by modifying the side residues accessible to the modifying agents under the given conditions, whose number in each protein is not quite so large. The set of chemical modification methods suitable for proteins is so far small compared with the scope of natural mutations.

In the reviews[2-5] devoted to the stabilisation of proteins and enzymes in solution which have been published in recent years, the influence of chemical modification on their stability is considered exclusively in phenomenological terms. Some workers assume that it is impossible to predict the effects of the modification.[5] The literature data on this question are not numerous, are incomplete, and are characterised by differences between the criteria used to define the stability of proteins, which hinders their comparison. In the present review the literature and the authors own results concerning the influence of chemical modification on the stability of proteins and enzymes is analysed, which made it possible to formulate certain general rules and the mechanism governing the variation of the stability of biomacromolecules as a result

of the chemical modification of their functional groups. The knowledge of these rules can help investigators to achieve success in the formation of enzyme preparations with a specified stability, having correctly selected the method of modification. From the theoretical standpoint, this is one of the important approaches to the elucidation of the interrelation between the structure and stability of biomacromolecules.

The analysis of studies of the influence of chemical modification on the stability of proteins and enzymes is preceded by the consideration of the main factors which determine the stability of the macromolecules in solution and the possible interrelation between the stability and structural parameters of macromolecules.[6,7]

II. THE STABILITY OF BIOMACROMOLECULES AS A FUNCTION OF THEIR STRUCTURE

1. The Principal Structural and Physicochemical Factors Determining the Stability of Protein Macromolecules in Solution

The native conformation of a protein having the minimum Gibbs free energy G_n under the given physical conditions consists of a three-dimensional structure, determined by the aminoacid sequence and the given microenvironment,[8] which exhibits the flexibility and internal dynamics essential for the manifestation of the functional activity of the protein.[9] Analysis of the three-dimensional structutes of a set of globular proteins have shown that all the aminoacid residues can be divided into three types in terms of their location in the globule: (1) hydrophobic, located preferentially within the molecule (Cys, Ile, Leu, Met, Val, Trp, and Phe); (2) hydrophilic, located preferentially in the surface layer (Asp, Glu, Lys, Asn, Gln, Pro, Arg, Ser, Thr); (3) neutral and ambivalent, indifferent as regards location on the surface or within the inner region of the molecule (Ala, His, Gly, Tyr).[10,11] A tendency towards the preferential cooperation of some aminoacid residues with others is characteristic of proteins,[12,13] which leads to the formation of structural domains in the macromolecule: clusters of hydrophobic or hydrophilic aminoacids.[14,15] Thus a high degree of mutual cooperation has been discovered between the following pairs of residues: Glu–Lys, Met–Arg, Asn–Trp, Gln–Pro.[12]

The transition of the biopolymer, without rupture of covalent bonds, from the native state (N) in which it exhibits its functional activity *in vivo* or *in vitro*, to the denatured (D) state, in which the activity has been lost either reversibly or irreversibly is the denaturation transition.[16,17] The principal feature of a cooperative system is the interaction between individual units whose energy is greater than the energy of thermal movement (kT).[18] The energy of the cooperative interaction is decisive for the operation of a particular kinetic mechanism of the cooperative transition from a disordered to a random state. Three types of interactions are possible in the system: (1) weak; (2) strong; (3) intermediate. In the first case the kinetics of the transition of the system from the ordered to the random state do not differ from those of the rearrangement of an individual unit. In the case of a strong interaction of the units, the system can rearrange as a whole only after an energy sufficient for the disruption of all the bonds of the system has accumulated simultaneously via a fluctuation process. Such transitions (in particular, the fusion of solids) are distinguished by high activation energies. The third, intermediate type of interactions occurs in proteins and the denaturation transition in a protein proceeds via a cooperative mechanism. Nevertheless, proteins resemble solids more closely than liquids and the enthalpy of fusion of the protein structure is a significant factor governing the stability of proteins.[19]

In order to describe the denaturation transition between the N and D states, the "all or nothing" mechanism, put forward *a priori*, is most frequently employed.[20] For the transition to be correctly analysed from the standpoint of the theory of two states and to obtain the true thermodynamic parameters of the transition, the transition must satisfy a number of tests, formulated by Brandts.[20] According to a large number of experimental data, the theory of two states can be used to a first approximation for virtually all globular proteins of small size.[7]

The change in the Gibbs free energy ΔG_{den} on complete and reversible uncoiling of the protein can serve as a measure of the stability of the latter:[6,7]

$$\Delta G_{den} = G_d - G_n,$$

where G_n and G_d are the free energies of the native and denatured forms, ΔG_{den} is the free energy of the stabilisation of the protein, and $a - \Delta G_{den}$ the free energy of its destabilisation. The numerical value of ΔG_{den} for the protein macromolecule is measured as a rule under the conditions involving the disruption of its native structure under the influence of heating, a change of pH, the addition of organic solvents, etc. This quantity is therefore significant only in relation to a specific type of denaturation.[7]

If the denaturation process is reversible, then ΔG_{den} is determined by measuring the constants for the equilibrium between the native and denatured forms of the protein, or by measuring the heat of denaturation with the aid of a scanning microcalorimeter. In the literature, the stability of the proteins is frequently characterised by the average temperature of the transition to the denatured state T_{den} (or T_m), at which 50% of the protein has been denatured and $\Delta G_{den} = 0$, by the temperature of the maximum stability of the protein T_{max} at which ΔG_{den} is a maximum (Fig.1), or by the average concentration of the denaturing agent, etc. In the case of irreversible denaturation (as a consequence of secondary processes) the kinetic stability of proteins is frequently characterised by the rate constants k_{in} for the change in any one property of the protein (the circular dichroism and ultraviolet spectra, fluorescence, and in the case of enzymes also their activity). In the general case the retention of the enzymic activity may not be identical with the stability of the entire protein globule.

The stability of a protein in solution is determined by a number of factors associated with the structural characteristics of the molecule.[20,21] An increase of the conformational entropy (~2–6 e.u. per uncoiled residue) decreases ΔG_{den}. The hydrogen bonds between the peptide groups in the biomolecule (the energy of a single bond is ~1.4 kcal mol^{-1})[17] increase ΔG_{den}.

Depending on the pH of the medium, the long-range electrostatic interactions of the charged groups on the surface of the protein can either stabilise (at pH close to the isoelectric point) or destabilise (at extreme pH values) the native conformation of the macromolecule. The hydrophobic interaction of the non-polar side residues stabilises the native conformation of proteins in aqueous solutions (the ΔG for the system decreases by ~2.8 kcal mol^{-1} when the aliphatic side residue is transferred from water to a non-polar solvent[22]). The intramolecular salt bonds (the energy of a single bond is ~1–3 kcal mol^{-1}), which can be formed either in the form of single electrostatic "fastenings" or within the composition of a spatially limited cluster consisting of several groups of charges of different sign, stabilise the native conformation of the protein. In the clusters a single ionogenic group can be involved in two, three, or four ionic interactions.[23–29]

Specific covalent cross-links in a polypeptide chain (in particular the S–S bonds) stabilise proteins not only as a result of a decrease of the entropy of the uncoiling of the globule[6] but also as a result of the enthalpy contribution (~1.8 kcal mol^{-1} per S–S bond[30]). Prosthetic groups form covalent, ionic, or coordinate bonds with the protein and stabilise the macromolecule as a whole.[31,32] Coordinate bonds involving Ca^{2+}, Mg^{2+} and Zn^{2+} metal ions are very important for the stabilisation of the native conformation of many protein molecules.[33,34]

Thus the total free energy of the denaturation of the protein ΔG_{den} includes the sum of the energies of all the types of interactions indicated above. The stability of the native conformation of a protein is achieved as a result of the displacement of the enthalpy and entropy functions along the temperature scale (Fig.1)[6] and reflects the fine balance between the stabilising and destabilising contributions of interactions of different types. At physiological temperatures, the ΔG_{den} of different globular proteins differ insignificantly and vary from 5 to 15 kcal mol^{-1}.[7] However, even a slight change in the balance between different interactions in the protein can greatly alter its stability, as will be seen below when the experimental data for stabilised proteins and enzymes are considered.

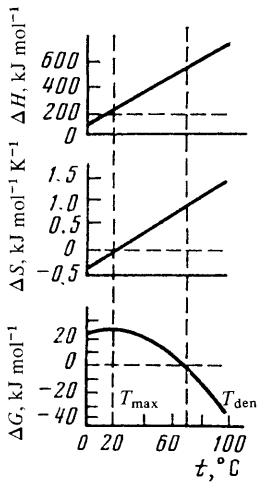


Figure 1. Temperature variation of the enthalpy, entropy, and free energy (ΔG_{den}) of denaturation of cytochrome b_5 (pH 7.4).[6]

Analysis of the principal energy characteristics of the protein structure shows[6] that (1) the protein should be stable under specific external conditions in order to retain its specific structural and functional properties; the energy reserves ensuring the stability of the protein should therefore greatly exceed RT—the minimum necessary value; (2) the protein should not be unduly "rigid", i.e. the structural changes in the course of the functioning of the protein should occur without much energy expenditure and at the same time the protein–water system should be capable of energy exchange in the course of its functioning without its breakdown; (3) since the stability of the protein is not correlated with its molecular weight, the size of the macromolecule should be the smallest possible to ensure its coiling up, transport, and functioning. This principle is realised by the formation of intramolecular domains or a subunit structure.[7] In contrast to the view that the protein structure is "rigid", which was held previously on the basis of X-ray diffraction data, thermodynamic data confirm the existence of fluctuations in the protein structure.[35] The amplitudes of the fluctuations of the atoms about their mean values are greater for less stable proteins and smaller for more stable proteins.[36] In conformity with the proposed mechanism of the dynamic stabilisation of the protein structure,[37] the internal mobility of the clusters of hydrophobic aminoacid residues in the macromolecule is responsible for the overall stability of its native conformation.[38]

The kinetic stability of the protein ($\Delta G^{\neq}_{den}$) is characterised by the inactivation constant k_{in} and the activation parameters determined from the temperature dependence of k_{in}. The kinetic and thermodynamic parameters of the denaturation of proteins vary in parallel as the denaturation conditions are altered,[20,39] which shows that the intramolecular interactions responsible for the thermodynamic stability (ΔG_{den}) determine also the kinetic stability ($\Delta G^{\neq}_{den}$) of proteins.

One of the commonest types of denaturation is thermal denaturation, on which attention has been concentrated in this review. An increase of temperature has different effects on the intramolecular interactions in proteins (Fig.2): (1) the degree of structure formation in water diminishes and up to about 60 °C the strength of the hydrophobic interactions increases; (2) the conformational entropy increases, which makes it possible to attain protein conformations with a higher free energy, i.e. more uncoiled forms of the macromolecule; (3) other intramolecular interactions stabilising the protein (salt, coordination, etc.) are weakened.[40]

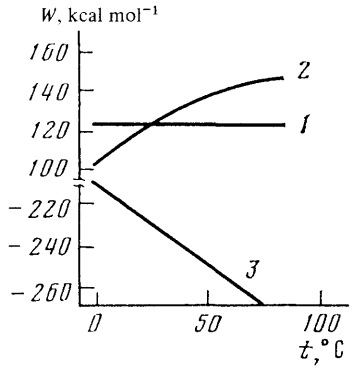


Figure 2. The influence of temperature on the overall contribution W of various factors to ΔG_{den} for native chymotrypsinogen: 1) hydrogen bonds; 2) hydrophobic binding; 3) conformational entropy.[40]

For the majority of globular proteins, the temperature dependence of ΔG_{den} is described by curves (Figs.1 and 3) which pass through a maximum (ΔG^{max}_{den}) at the temperature of the maximum stability of the protein T_{max} and which have upper (T_{den}) and lower temperature limits of the stability of the protein (at $\Delta G_{den} = 0$). T_{max} is usually appreciably lower than physiological temperatures[7] and for many globular proteins is in the range from −3° to +10 °C, which is important for practical purposes and makes it possible to store proteins for a long time at these temperatures.[2] With increase of temperature up to 55 °C, the exposure of the internal aminoacid residues to the solution and the increase of the mobility of the individual sections of the polypeptide chain lead to the reversible local expansion of the native protein macromolecule.[20,41] Above 55 °C, these changes

become irreversible and the protein assumes a fully uncoiled structure.

Water has a destabilising effect on the protein macromolecule. Practical experience has shown that lyophilised proteins keep much longer than in solution. When the water content is more than 0.75 g per gram of protein, the degree of hydration does not affect T_{den} and ΔH_{den} for the protein.[42-44] For a water content below 0.75 g per gram of protein, ΔH_{den} gradually diminishes and T_{den} increases slightly. When the water content is below 0.4 g per gram of protein, T_{den} rises sharply by 30–40 °C. These facts reflect the existence in proteins of various types of bound water. A small number of water molecules are strongly bound to the protein and the system can be regarded as a single whole. The less strongly bound water is distributed over the entire surface of the globule, interacting with its hydrophilic residues. The next layer is transitional in relation to water in bulk.[43] The largest contribution to ΔH_{den} for the protein comes from the ΔH for the disruption of the hydrophobic contacts when the protein is uncoiled, i.e. the ΔH for the ordering of the water molecules around the exposed non-polar groups of the protein. With decrease of the water content, the degree of hydration of the non-polar residues in the denatured state of the protein diminishes, which entails a decrease of ΔH_{den} for the protein.[44] Since the uncoiling of the protein molecules during denaturation is due to the competition between water molecules and protein residues for hydrogen bonds, in the presence of a very low water content the protein molecule is not fully uncoiled.

Although a correlation between the physicochemical properties of proteins and their stability has not been discovered, analysis of data for a large number of proteins suggested the following:[7] (1) in the course of their functioning, proteins forming complexes with other biomacromolecules have as a rule low values of ΔG_{den} (α-lactalbumin, cytochromes *c* and b_5); (2) proteins reacting with low-molecular-weight compounds or with individual sections of other macromolecules have high values of ΔG_{den} (myoglobin, various hydrolytic enzymes).

On the basis of numerous data, a satisfactory correlation has been observed between the stabilities of proteins *in vivo* and *in vitro*.[45-48] This is due to the fact that one of the causes of protein and enzyme inactivation in the cell is the proteolysis of their denatured (uncoiled) conformers, the rate of which is limited by the rate of uncoiling of the native conformation.[47] The turnover rate of the protein *in vivo* is correlated with its T_{den} and with its stability in relation to acid and mechanical denaturation.[46,48] The stability of certain proteins is satisfactorily correlated with the metabolic rate.[49]

However, overall, the thermal stability of the protein is not correlated either with ΔG_{den}, measured under standard conditions, or with T_{den}, i.e. these quantities cannot by themselves serve as objective measures of thermal stability when different proteins are compared.[1,7] For example, cytochrome *c* and lysozyme have the same T_{den} but their maximum values of ΔG_{den} differ approximately by a factor of two. At certain temperatures α-chymotrypsin and lysozyme have almost identical ΔG_{den}, but their T_{den} differ by 20 °C (Fig.3). The thermal stability of the protein is correctly described only by the complete temperature dependence of ΔG_{den} over a fairly wide temperature range. It is particularly important to bear this in mind on comparing the stability of the modified or immobilised enzyme with that of the native enzyme, because the ratio of the ΔG_{den} at a single fixed temperature cannot be extrapolated to other temperatures.

Thus the knowledge of the principal factors responsible for the stability of the native conformation of the protein in solution makes self-evident the general principles by which one should be guided in obtaining protein and enzyme preparations with increased stability over a specific temperature range: (1) the introduction of additional intramolecular bonds (salt and hydrogen bonds) and the enhancement of hydrophobic interactions will increase ΔG_{den} for the protein (one additional bond with an energy of 1–3 kcal mol^{-1} can significantly increase the stability of the protein); (2) a decrease of the conformational mobility of fragments of the polypeptide chain as a consequence of the formation of additional intramolecular (covalent or non-covalent) "cross-links" in the globule (additional S–S bonds, coordinate bonds with metal ions, etc.) will diminish the conformational entropy[6] and hence will increase ΔG_{den}.

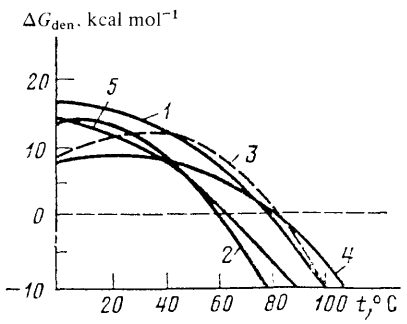


Figure 3. Temperature variation of the free energies ΔG_{den} for globular proteins measured microcalorimetrically: 1) lysozyme; 2) α-chymotrypsin; 3) metmyoglobin; 4) cytochrome c; 5) ribonuclease.[21]

As will be shown below, these principles hold in nature in the formation of proteins and enzymes with increased stability (enzymes from thermophilic microorganisms) and under practical conditions in the preparation of stabilised enzymes by their chemical modification or immobilisation.

2. Relation between the Stability of Biomacromolecules and Their Primary, Secondary, and Tertiary Structures

In order to discover the principal structural factors related quantitatively to the stability of biomacromolecules, a number of attempts have been made in recent years to find a correlation between the stability and the primary, secondary, and tertiary structures of proteins. For this purpose, the aminoacid compositions of proteins with different stabilities were compared and studies were made of the physicochemical causes of the increased stabilities of proteins and enzymes isolated from thermophilic sources and also of the influence of point mutations on the stability of proteins and enzymes.

(a) Correlation between the primary structure and the stability of proteins. An empirical relation between T_{den} and the hydrophobic index X_1 and the average volume of aminoacid residues in the protein X_2 has been discovered for 14 proteins:

$$T_{den} = 226.81 - 0.01270X_1 + 3.847X_2 .$$

It is seen that the main contribution to T_{den} comes from the average volume of the aminoacid residues X_2 and not from their hydrophobic properties. The Glu residues stabilise proteins to the maximum extent, while the Ser residues

destabilise them.[50] However, for a large number of proteins a correlation between T_{den} and X_2 has not been found.[51]

The correlation between the hydrophobic properties and thermal stability of proteins proposed by Bigelow[52] was not subsequently confirmed.[53]

A clear relation has been observed between T_{den} and the ratio S_n/S_d, where S_n and S_d are the surface areas of the protein accessible to the solvent in the native and denatured states respectively: $S_n = 11.116\,M^{2/3}$, while $S_d = 1.44\,M$ (M is the molecular weight of the protein). For 20 of the proteins investigated, T_{den} increases linearly with increase of S_n/S_d, i.e. with decrease of M. The ratio S_n/S_d diminishes with increasing M and there is a decrease of the thermal stability of the protein. For the same ratio S_n/S_d, the quantity T_{den} is greater for subunit proteins than for monomeric proteins. The thermal stability of a long polypeptide chain can be increases in the following way: (1) by the association of the globular subunits to form an oligomer; (2) by coiling up with formation of a multiplicity of globular domains. In such cases S_n/S_d (and T_{den}) increases for an unchanged molecular weight M. The deviations from linearity for certain proteins can be accounted for by the influence on their stability of intramolecular interactions such as those involved in S–S bonds in the binding of metal ions, cofactors, etc.[53]

The microstability of the protein globule differs from its macrostability G_{den} by the fact that the former characterises the local uncoiling of the protein and is determined from the rate of exchange of the protons in the inner part of the macromolecule with water.[54] The microstability, i.e. the "rigidity" of the protein globule, does not characterise the macromolecule as a whole. It depends on the degree of saturation of the protein by non-polar contacts and increases as the hydrophobic nucleus of the macromolecule grows. On the other hand, ΔG_{den} is independent of the hydrophobic properties of the protein globule and is directly related to the number of intramolecular cross-links, which diminish the conformational entropy of ΔS_{conf} of the uncoiling of the polypeptide chain (the binding of M^{n+} ions and cofactors has an analogous influence).[54]

The specific preferential cooperation of various aminoacid residues in proteins with one another, which has been found on the basis of their three-dimensional structure,[12,13] apparently determines the increased or reduced stability of a particular protein with increase of temperature.[55] Comparison of the T_{den} and the aminoacid compositions for a large number of proteins made it possible to establish a relation between the content of each aminoacid residue and T_{den} for the protein. All the aminoacid residues are divided into stabilising (positive correlation with T_{den}) and destabilising (negative correlation with T_{den}). A combination of charged and non-polar helical residues (I), namely Asp, Cys, Lys, GlU, Leu, Arg, Trp, and Tyr has the greatest stabilising effect, while a combination of neutral and short non-polar residues (II), namely Ala, Asn, Gly, Gln, Ser, Thr, Val, and Tyr has a destabilising effect. The overall correlation can be formulated by the equation

$$T_{den} = 64.46202 + 0.89432Y_1 - 0.59065Y_2,$$

where Y_1 and Y_2 are the percentage contents in the protein of the stabilising (I) and destabilising (II) aminoacid residues. Phe, Ile, Met, His, Asn, and Pro do not influence the stability of the protein.[55] The upper limit of the stability of the protein, corresponding to a 100% content of group I residues, is $T_{den} = 164.3$ °C, while the lower limit of the stability, corresponding to a 100% content of group (II) residues, is $T_{den} = 5.4$ °C. However, the proposed correlation between T_{den} and the aminoacid composition of the proteins is valid only for small compact monomeric proteins. Under these conditions, haem or S–S bonds have a lesser influence on the stability of the protein than its aminoacid composition.[55]

A disadvantage of all the correlations discussed above is that, firstly, they are valid only for a limited group of proteins and enzymes, which is as a rule the group for which the given correlation had been derived. Secondly, T_{den} has been used as a general criterion of thermal stability, but, as already mentioned above, it cannot serve as an objective measure of the stability of the protein over a wide temperature range (Fig.3). The determination of a simple thermal stability–temperature correlation is apparently impossible owing to the complex relation between ΔG_{den} for the protein and temperature:[7]

$$\Delta G_{den}(T) = \Delta H_{den}(T_{den} - T)/T_{den} - \int_T^{T_{den}} \Delta C_p \, d\,T + T \int_T^{T_{den}} \Delta C_p \, d \ln T.$$

In the future, it will probably be necessary to establish a relation between $\Delta G_{den}(T)$, and not T_{den} for proteins, and the structure of the macromolecules. In addition, by virtue of the multiplicity of the structural factors responsible for the stability of the native conformation of the protein, the existence of such a correlation is possible only for a limited number of isotypical globular proteins.

(b) Physicochemical causes of the increased stability of the enzymes derived from thermophilic sources. From the standpoint of the determination of the stability–structure function, comparison of the structures of proteins and enzymes isolated from thermophilic micro-organisms (t-enzymes) and exhibiting an increased thermal stability with their mesophilic analogues (m-enzymes), having structures similar to those of the t-enzymes, is more promising. Such a comparison makes it possible to discover the principal structural characteristics of t-enzymes responsible for their increased thermal stability.

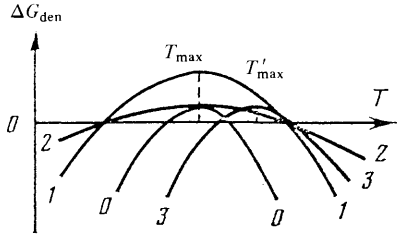


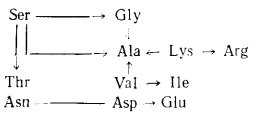
Figure 4. Hypothetical curves for the temperature variation of ΔG_{den} for globular proteins from thermophilic sources: *0*) mesophilic protein; 1) thermophilic protein with a higher value of ΔG_{den} (rise of curve *0*); 2) thermophilic protein with a higher temperature range of stability (the levelling off of curve *0*); 3) thermophilic protein with a displaced stability maximum (shift of curve *0* from T_{max} to T'_{max}).[60]

The thermal stability of microbial enzymes is correlated with the temperatures corresponding to the existence of the micro-organisms.[56] At low culture temperatures (<50 °C) m-enzymes are synthesised, while at high culture temperatures (>50 °C(t-enzymes are synthesised.[57,58] t-Enzymes are also stable in relation to other types of denaturation, namely denaturation by urea, guanidine hydrochloride, and organic solvents and under the influence of pH.[59]

The increased thermal stability of a t-protein compared with an m-protein can result from the operation of the following factors (Fig.4): (1) the increase of the activation energy for the denaturation process; (2) the increase of the free energy of denaturation ΔG_{den}; (3) the equalisation of the free energy of denaturation profiles; (4) a shift of the ΔG_{den} profile.[60] The stability of the majority of t-enzymes increases as a result of the higher position of the curve describing the temperature dependence of ΔG_{den} (from curve *0* to curve *1* in Fig.4). Additional hydrophobic, hydrogen, salt, and S–S linkages, which are present in t-enzymes but not m-enzymes, lead to such alteration of ΔG_{den}. On the other hand, ΔG_{den} for t-enzymes can vary in accordance with curve *2* (Fig.4) as for *t*-phosphoglycerate kinase.[60]

Thermophilic proteins and enzymes have high thermodynamic and kinetic stabilities. Since in terms of the absolute temperature scale, the difference between 35 °C (T_{den} for m-enzymes) and 80 °C (T_{den} for t-enzymes) is relatively small (~15%), even small differences between the activation energies and ΔG_{den} for t- and m-enzymes can lead to appreciable differences between their thermal stabilities for a small difference between their structures. Calculation shows that a decrease of k_{in} by a factor of ten at 70 °C requires an increase of ΔG_{den} by only 1.56 kcal mol^{-1}. In order to increase T_{den} from 35° to 45 °C for a polypeptide chain with $M = 35\,000$, it is necessary to increase the number of hydrogen bonds by only 3%. The differences between ΔG_{den} and $\Delta G^{\neq}_{den}$ for proteins amounting up to 10 kcal mol^{-1} can be obtained following the replacement of one or two aminoacid residues in the molecule.[53]

(c) The fundamental differences between the structures of enzymes from thermophilic and mesophilic sources. The fundamental differences between the aminoacid compositions of t- and m-enzymes have been discovered following a comparison of the aminoacid compositions of a large number of t- and m-enzymes. In relation to ferredoxins, glyceraldehyde-3-phosphate dehydrogenases, and lactate dehydrogenases, the following directions of the preferential exchange of aminoacid residues on transition from m- to t-enzymes have been discovered:[61]



The above changes enhance the hydrophobic properties of the residues and their capacities for helix formation and folding. Under these conditions, the volume of the internal residues increases somewhat and a more compact packing is achieved in the structure of the protein globule. The principal role of the stabilising additional ion pairs in these t-enzymes has been demonstrated on the basis of structural investigations.[62] A higher content of Ala and Gly and charged residues is characteristic of t-lactate dehydrogenase (LDH), while m-LDH contains more Ser, Thr, Gln, Asn, and polar residues. Although the content of hydrophobic residues is the same in the two enzymes, in the t-enzyme they exist only within the globule, while in the m-enzyme they are also present on the surface. The spatial dispositions of the charged and polar residues are also different in t- and m-LDH:[62] in t-LDH the charged residues are located only on the surface of the molecule, while in m-LDH they are also present inside it. Thus the distribution of the aminoacid residues in the t-LDH molecule is thermodynamically more favourable.

Analysis of the aminoacid compositions of 14 t-enzymes and 207 m-enzymes showed that the thermophilic enzymes contain more Gly, Arg, Glx but less Asx and Ser.[63] A positive correlation between the thermal stability and the ratio of Arg and Lys in the protein has also been noted.[64] Arginine is the most hydrophilic aminoacid and its location on the surface is more favourable compared with Lys. The resonance structure of the guanidinium ion enables it to form more than one bond with anionic residues. t-Enzymes are also characterised by a higher content of α-helices and of the β-structure than m-enzymes. The increased Glu content in t-enzymes increases their capacity to bind metal ions. It may be that this is one of the principal causes of the increased stability of t-enzymes.[63]

A positive correlation between the thermal stability and the aliphatic index of the protein A, determined from the formula

$$A = \chi_{Ala} + a\chi_{Val} + b(\chi_{Ile} + \chi_{Leu}),$$

where $a = 2.9 \pm 0.1$, $b = 3.9 \pm 0.1$, and χ represents the content of Ala, Val, Ile, and Leu residues in the protein (in molar percentages), has been established for 34 t-enzymes and 208 m-enzymes. Since the content of the above residues in t-enzymes is much higher than in m-enzymes, each t-enzyme has a greater aliphatic index than its mesophilic analogue.[65]

Comparison of the tertiary structures of t- and m-enzymes revealed two additional salt and hydrogen bonds in t-ferredoxin.[53,66] The increased stability of t-triose phosphate isomerase is due to additional salt and hydrophobic linkages between the subunits.[66] Two additional intersubunit and intrasubunit salt linkages stabilise t-glyceraldehyde-3-phosphate dehydrogenase,[21,67–69] while additional salt linkages, hydrophobic interactions, and bonds with additional Ca^{2+} ions are responsible for the stabilisation of thermolysin.[70–72] The additional salt linkage between Asp (201) [Asn(201) in the m-enzyme] and the His residue increases the activation energy for the thermal denaturation of t-tyrosinase.[73] Among the ten ion pairs in t-LDH, eight are formed by Arg residues, while in different m-LDH only 2, 4, or six ion pairs, containing Lys instead of Arg, have been found.[62] The principal role in the stabilisation of t-LDH has been attributed to additional surface salt linkages formed by Arg residues and also to an enhancement of the intramolecular hydrophobic interactions as a consequence of the decrease of the number of hydrophobic residues on the surface of the globule and of its increase within the globule.[62] The greater thermal stability of other thermophilic enzymes, whose tertiary structures have not been studied in detail, compared with m-enzymes has been explained by the greater number of hydrogen bonds and the stronger intersubunit interaction in the case of enolase,[74,75] the greater number of intramolecular cross-links (S–S bonds) in the case of the iron–sulphur protein[76] and glutamine synthetase,[77] the protective effect of the surface carbohydrates in β-glucosidase,[78] or the change of conformation in the case of dehydrogenase.[79]

Thus the high thermal stability of the enzymes from thermophilic microorganisms is due to the exceptionally small number of additional (compared with m-enzymes) bond both within the macromolecule and on its surface. For the majority of t-proteins, these are mainly salt linkages, which follows from a comparison of the tertiary structures of t- and m-enzymes.

(d) Point mutations and the stability of the protein. The study of the influence of point mutations (which alter only 1–2 aminoacid residues in the polypeptide chain) on the stability of the protein can also yield valuable information about the relation between structure and stability. In contrast to t-enzymes, where the natural selection of the most

stable form from the multiplicity of mutant forms takes place, the artificial mutations are random in their influence on the stability of the protein, which relates them to chemical modification.

The replacement of a single Trp (138) residue by Tyr in the lysozyme of the T4 phage (a polypeptide without S–S bonds) diminishes ΔG_{den} (and T_{den}) over the entire temperature range from 0° to 60 °C by 2–3 kcal mol^{-1} (Fig.5).[80] Here ΔH_{den} diminishes by 20 kcal mol^{-1}. The replacement of a further two Trp residues by Tyr diminishes ΔG_{den} to a still greater extent at all the temperatures studied (Fig.5). Although the overall conformation of the lysozyme hardly changes after the mutations, one of the possible explanations of the marked decrease of ΔH_{den} after the mutation and of its compensation by the simultaneous decrease also of ΔS_{den} might be the local uncoiling of the molecule.[80]

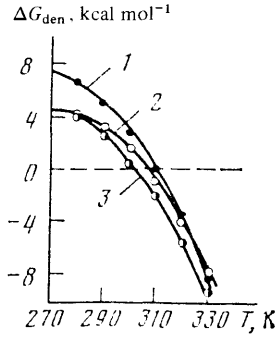


Figure 5. Temperature variation of ΔG_{den} for the native (curve *1*) and mutant (curves *2* and *3*) forms of lysozyme at pH 2.0: 2) Trp (138) replaced by Tyr; 3) Trp (138), (126), and (158) replaced by Tyr.[80]

The single-point replacements of Glu (128) by Lys, of Arg (96) by His, and of Ala (146) by Thr in the T4 phage lysozyme do not alter its tertiary structure but diminish T_{den} by 5°, 14°, and 9° respectively.[81,82] The first mutation increases ΔH_{den}, while the second and third diminish it. The greatest destabilising effect (T_{den} diminishes by 14°) is shown by the replacement of Arg (96) by His. According to the authors, this can be explained by a weakening of the hydrophobic interactions in the molecule and the possible rupture of the α-helix between the aminoacid residues in the 82–90 position.[81]

The replacement of Glu (49) by Met in the α-subunit of tryptophan synthetase from *E.coli* yields a mutant which is twice as stable (at 58 °C) in relation to thermal denaturation and the denaturation by urea.[82] The spatial structure of the enzyme does not then change. According to the authors, the enhancement of the hydrophobic interactions in the mutant following the replacement of the hydrophilic Glu in the hydrophobic nucleus by Met is responsible for the observed stabilisation effect. The nature of the aminoacid residue in the 49-position revealed an interesting relation: the replacement of the charged Glu (49) by the uncharged polar residues Tyr, Ser, and Gln increases the stability of the α-subunit of tryptophan synthetase in relation to guianidine hydrochloride at pH 9.0, while at pH 7.0 and 5.5 it destabilises the enzyme, which is shown most strikingly in the case of Gln.[84] On the other hand, the replacement of Glu (49) by the hydrophobic aminoacid residues Met and Val greatly increases (by 5 kcal mol^{-1}) the stability of tryptophen synthetase relative to guanidine hydrochloride at all pH (particularly at pH 7.0 and 9.0). According to the authors,[83] Glu (49) is in a hydrophobic environment and any diminution of the hydrophilic properties of the residue in the 49-position will therefore naturally induce an increase of the stability of the enzyme. The replacement of Gly (211) in the α-subunit of tryptophan synthetase by Arg or Glu increases somewhat the thermal stability of the enzyme (at 57.8 °C ΔH_{den} increases by 0.1 and 0.6 kcal mole^{-1}, while T_{den} increases by 0.2° and 1.8 °C respectively).[85] On the other hand, ΔH_{den} increases by 17 and 15 kcal mol^{-1} as a result of these mutations. It has been shown that the conformations of the native enzyme and the two mutants are similar. The segment of the chain containing Gly (211) is apparently located on the surface of the molecule and does not participate in any appreciable interactions, so that the replacement of Gly by the more bulky charged Glu and Arg residues induces only small changes in the non-covalent interactions on the surface of the protein.[85]

Studies on point mutations have shown that even the replacement of one aminoacid residue induces an appreciable change in the stability of the protein. Depending on the location of the replaced residue, its immediate environment, and the nature of the substituting residue, the stability either increases or decreases after the mutation as in the case of chemical modification (this will be demonstrated in the next Section). Mutations increasing the polarity within the protein globule (the hydrophobic nucleus) diminish its stability, while those which enhance its hydrophobic properties stabilise it. The mutations of the surface aminoacid residues have only a weak influence on the stability of the macromolecule.

In conclusion it must be emphasised that the stability of the protein is very sensitive not only to changes in its conformation but also to slight variations in the primary structure (as can be seen in relation to point mutations). Therefore a change in the stability of the protein (in particular, its thermal stability) constitutes a sensitive test for the changes in the structure of the protein, which may be below the limits of the resolution of both structural analysis and other physicochemical methods.[7,86]

III. THE MECHANISM OF THE CHANGES IN THE THERMAL STABILITY OF PROTEINS AND ENZYMES AFTER THE CHEMICAL MODIFICATION OF THEIR FUNCTIONAL GROUPS

The chemical modification method is used widely for the identification of the groups in the active centres of enzymes and for the investigation of the topography and conformations of biomacromolecules.[87] In connection with the problem of the stabilisation of biocatalysts, increasing attention has been devoted in recent years to the chemical modification of the functional groups of the protein which do not enter into the active centre.[2–4] Only the surface groups of the protein or those near the surface under the given conditions are as a rule accessible to chemical modification. Depending on the conditions (pH, temperature, etc.), the number of surface groups, i.e. groups accessible to the solvent, can vary.

The reactive groups of the protein can be divided into three components: (1) acid groups (the COOH groups at the C-ends and in the Asp and Glu residues); (2) basic groups (the α-NH_2 groups at the N-ends, the Lys and Arg residues, and the OH groups in the Tyr, Ser, and Thr residues and in the carbohydrates in glycoproteins); (3) neutral groups (the imidazole group in His).[88] The reagents most frequently used for the chemical modification of proteins and enzymes in order to stabilise them or alter their structure are listed in Table 1.

Table 1. The changes in the structure and stability of proteins and enzymes as a result of the chemical modification of their functional groups.

Protein	Modifying agent	Modified residue[a]	Derivatives obtained	Degrees of modification: not influencing structure and thermal stability	Degrees of modification: increasing thermal stability[b]	Degrees of modification: uncoiling and destabilizing the molecule[b]	Refs.
Bovine serum albumin	Succinic anhydride[c]	Lys (59)	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_2CH_2COO^{\ominus}$	Up to 60% (up to 30–34 residues)	—	more than 80%	[90—92]
	Methyl acetimidate[c]	»	$E-NH_3^{\oplus} \rightarrow E-NHC(NH_2^{\oplus})CH_3\ Cl^{\ominus}$	up to 100%	—	—	[92]
	Butyric anhydride	»	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_2CH_2CH_3$	up to 90%	—	more than 90%	[93]
Human immunoglobin G	Succinic anhydride[c]	Lys[?] (90)	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_2CH_2COO^{\ominus}$	up to 87% (up to 78 residues)	—	more than 87% (expansion of molecule, decrease of β-folds owing to electrostatic repulsion)	[90]
	Citraconic anhydride[c]	»	$E-NH_3^{\oplus} \rightarrow E-NHCOCH=C(CH_3)-COO^{\ominus}$	Low degrees of modification	—		[94]
	Potassium iso-cyanate[c]	»	$E-NH_3^{\oplus} \rightarrow E-NHCONH_2$	up to 100%	—	—	[94]
	Acetylacetone[c]	Lys (29)	$E-NH_3 \rightarrow E-N=C(CH_3)CH_2COCH_3$	—	—	from 1 to 6 Lys	[95]
Leucine-binding protein	»	Arg (7)	$E-NHC(NH_2^{\oplus})NH_2 \rightarrow E-NH-C(N-C(CH_3)=CH-C(CH_3)=N)$	up to 3 Arg	—	—	[95]
11S globulin	Acetic anhydride[c]	Lys[e]	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_3$	up to 21%	—	more than 21%	[96]
Ovalbumin	Succinic anhydride[c]	Lys[e] (19)	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_2CH_2COO^{\ominus}$	Up to 66%	—	More than 66% (uncoiling of protein globule)	[97]
Cytochrome *c*	Tetranitromethane	Tyr (4)	$E-C_6H_4-OH \rightarrow E-C_6H_3(NO_2)-OH$	—	1 residue (increase of T_{den})	2 residues (extensive uncoiling	[98]
Cytochrome *c*-552	Acetic anhydride[c]	Lys[e] (4)	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_3$	Up to 100%	—	—	[99]
Horse cytochrome *c*	4-Chloro-3,5-dinitrobenzoic acid	Lys (19)	$E-NH_3^{\oplus} \rightarrow E-NH-C_6H_2(NO_2)_2-COO^{\ominus}$	2 residues (7 and 60) remote from top and bottom of of haem crevice	2 residues (27 and 72) on frontal surface near exposed portion of haem moiety (formation of new surface salt bonds)	Lys (13) on top of haem crevice [rupture of Lys (13)–Glu (90) salt bond greatly widens haem crevice); lysines 8, 86, and 87 on top of crevice (destabilisation as a consequence of decrease of electrostatic potential in this region)	[29, 100, 101]
	Succinic anhydride	Lys	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_2CH_2COO^{\ominus}$	Up to 95% (up to 18 residues), stability does not change relative to denaturation by urea	—	100%	[102]
	Maleic anhydride[c]	Lys	$E-NH_3^{\oplus} \rightarrow E-NHCOCH=CHCOO^{\ominus}$	—	—	Modification of all 19 residues	[103]
Myoglobin	Bromoacetate	His (12)	$E-C_3H_3N_2^{\oplus} \rightarrow E-C_3H_3N_2-N-CH_2-CO-OCH_3$	Up to 50–58% (6–7 residues)	—	—	[104]
	Iodoacetamide		$E-C_3H_3N_2^{\oplus} \rightarrow E-C_3H_3N_2-N-CH_2-CO-NH_2$	Up to 50–58% (6–7 residues)	—	—	[104]
β-Lactoglobulin	Succinic anhydride	Lys[e] (16)	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_2CH_2COO^{\ominus}$	—	1–3 residues (small increase of stability relative to denaturation by urea)	From 4 to 10 residues (lower stability); more than 10 residues (uncoiling of protein also in absence of urea)	[102]
Ribonuclease	Succinic anhydride	Lys[e] (11)	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_2CH_2COO^{\ominus}$	Up to 100% (relative to denaturation by urea)	—	—	[102]

Table 1 (contd.)

Protein	Modifying agent	Modified residue[a]	Derivatives obtained	Degrees of modification: not influencing structure and thermal stability	Degrees of modification: increasing thermal stability[b]	Degrees of modification: uncoiling and destabilizing the molecule[b]	Refs.
	Acetic anhydride	Lys	$E-NH_3^{\oplus} \rightarrow E-NHCCH_3$ (O)	—	Low degree of modification: some stabilisation	All 11 residues	[105]
	N-Acetylhomocysteine thiolactone	Lys	$E-NH_3^{\oplus} \rightarrow E-NHCCHCH_2CH_2SH$ (O; NHCOCH$_3$)	—	8 residues: increase of stability	—	[106]
Glucoamylase	Acryloyl chloride	Lys	$E-NH_3^{\oplus} \rightarrow E-NHCCH=CH_2$ (O)	Up to 66 residues	—	More than 66% of residues: stability falls sharply; 100% of residues: stability diminishes by a factor of 2.5 at 65 °C	[107]
Horseradish peroxidase	Acetic and oenanthic anhydrides	Lys (6), OH groups of Tyr(5), Ser (25), Thr (25), and carbohydrate residues	$E-NH_3^{\oplus} \rightarrow E-NHCOCH_2 \cdot R$; $E-OH \rightarrow E-OCOR$	Up to 2 Lys residues, up to 30 surface OH groups	3–4 Lys residues (below 75 °C, k_{in} falls with increase of degree of modification); stabilisation as a result of increase of strength of haem–protein bond	6 Lys residues, more than 30 OH groups (when internal OH groups are also involved)	[34, 108, 109]
	Trinitrobenzenesulphonic acid	Lys (6)	$E-NH_3^{\oplus} \rightarrow E-NH-SO_2-C_6H_2(NO_2)_2$	—	3 residues, same effects as in previous case	6 residues: decrease of stability (weakening of haem-protein bond)	[108]
α-Amylase	*p*-Nitrophenyl acetate	Lys	$E-NH_3^{\oplus} \rightarrow ENHCOCH_3$	—	—	With increase of degree of modification from 1.5 to 11.5 residues, the protein conformation approaches that of denatured form, k_{in} increases below 67 °C, and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ diminish	[110, 111]
Myosin	β-Naphthoquinone-4-sulphonic acid	Lys			Thermal stability increases with increase of degree of modification from 1 to 15 residues	—	[112]
Lactate dehydrogenase	*O*-Methylisourea	Lys	$E-NH_3^{\oplus} \rightarrow E-NH-C(=NH_2^{\oplus})-NH_2$	—	4–5 residues per subunit: sharp increase of stability (formation of stronger salt bonds between COO^- and guanidine groups introduced; from 5 to 15 residues slight increase of stability	—	[113]
Lactate dehydrogenase	Methyl 4-hydroxy-3-nitrobenzimidate	Lys	$E-NH_3^{\oplus} \rightarrow E-NH-C(=NH_2^{\oplus})-C_6H_3(OH)(NO_2)$		With increase of degree of modification from 5 to 30 residues, stability increases by a factor of 2–6 at 60 °C		[114]
α-Chymotrypsin	Succinic anhydride	Lys[c] (17)	$E-NH_3^{\oplus} \rightarrow E-NHCCH_2CH_2CO^{\ominus}$ (O; O)	Up to 50% modification; for 100% modification the structure is close to native structure, slight increase of stability	From 60 to 95%: sharp increase of thermal stability (~20 times)	More than 95%: sharp fall of stability (approximately down to that of native protein)	[115, 116]
	Acrolein (with subsequent reduction by $NaBH_4$)	Lys	$E-NH_3^{\oplus} \rightarrow E-NH_2^{\oplus}-CH_2CH=CH_2$	Up to 50%: slight increase of stability	From 50 to 95%: sharp increase of thermal stability (~120 times for 95% modification); cause: change in conformation after modification	More than 95%: sharp fall of stability (down to that of native protein)	[116]

[a] The total number of given residues in the protein is indicated in brackets.

[b] The physicochemical causes responsible for the given change in the structure and stability of the protein are indicated in brackets.

[c] The thermal stability was not investigated in these studies.

[d] Alkylation entails the modification, apart from the NH_2 groups of Lys, of the SH groups of Cys and OH groups of Tyr, Ser, and Thr,[117,118] which was not taken into account by the authors of the given investigations.

[e] E = enzyme or protein.

Carboxylic acid anhydrides and chlorides, iminoesters, aldehydes, and chloro- and sulpho-derivatives of tri- or di-nitrobenzenes are employed for the modification of the amino-groups. The Arg residues are modified by various diketones. The nitration or iodination of proteins lead to the modification of the Tyr and Trp residues. The Ser and Thr residues and the OH groups of the carbohydrate residues in glycoproteins are acylated by acid anhydrides and chlorides. Bromoacetate and iodoacetamide modify the His residues. The carboxy-groups in the Leu and Asp residues are modified by means of carbodiimides or the Woodward reagent.[119,120] The above groups of proteins are also used in covalent immobilisation and the alteration of the stability of the biocatalyst can be to a large extent associated with the modification of its primary structure.

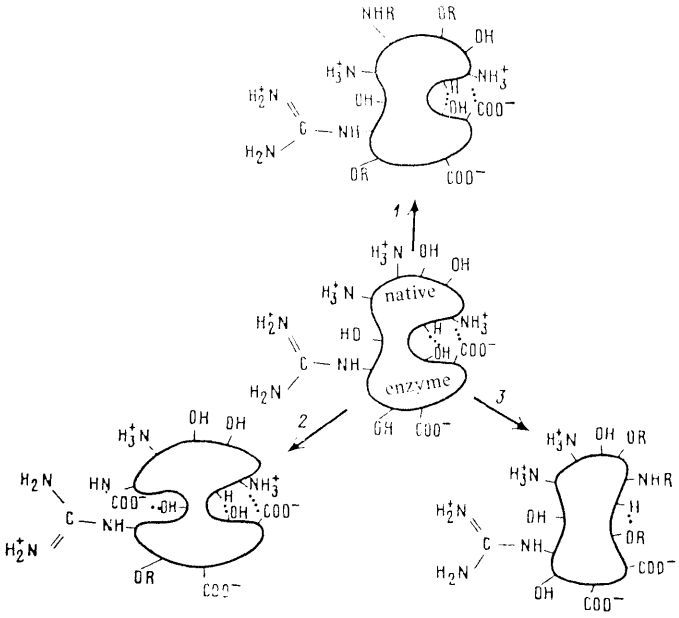


Figure 6. Schematic representation of various types of functional groups of enzymes; types of groups modified: 1) type I; 2) type II; 3) type III.[121]

The same functional groups of proteins and enzymes play different roles in the stabilisation of their native structures depending on their location in the globule and on whether or not they are involved in intramolecular interactions stabilising or destabilising the macromolecule. It is possible to isolate three types of functional groups accessible to modification (Fig.6). *Functional groups of type I* are located on the surface of the globule. These are effectively hydrated polar or charged groups, which do not interact with one another under the given conditions and interact only with the solvent or with ions from the solution. *Functional groups of type II* are located on or near the surface of the protein. In the native enzyme they have an unfavourable environment (charged groups in a hydrophobic environment or in an environment of groups bearing like charges) and destabilise the protein globule. The number of groups of this type in the protein is usually small. *Functional groups of type III* are remote from the surface of the globule and form intramolecular salt or hydrogen bonds stabilising the enzyme. These groups are inaccessible to modification under the usual conditions and are modified only for a loosened conformation of the protein (at an elevated temperature, at extreme pH values, or in the presence of organic solvents).

Chemical modification of functional groups of different types has different effects on the structure and stability of the enzyme. The observed effect also depends on the nature of the residues introduced into the enzyme on modification. Modification of groups of type I in the general case causes little alteration in the conformation and stability of the enzyme regardless of the dependence on the nature of the modifying agent and the degree of modification. If a large number of bulky hydrophobic residues or residues bearing a like charge are introduced into the enzyme at the same time, partial uncoiling of the molecule and its destabilisation can take place. In the same case, when the residues introduced form additional non-covalent bonds (salt and hydrogen bonds) with the neighbouring groups of the protein, the stability of the enzyme can actually increase. A large stabilisation effect is to be expected on modification of groups of type II when the interactions destabilising the native conformation are eliminated. On modification of groups of type II, the degree of modification, the charge, and the hydrophobic properties of the residues introduced actually exert a great influence on the thermal stability. Modification of groups of type *III* should diminish the thermal stability of the enzyme as a result of the breakdown of the intramolecular bonds stabilising its native conformation. The structure of the enzyme approaches the denatured structure after such modification.

Consequently, depending on which role particular functional groups play in maintaining the native structure of the enzyme, their modification either does not influence the thermal stability (groups of type I) or stabilises (groups of type II) or destabilises (groups of type III) the enzyme. It is to be expected that for each specific enzyme the ratios of the groups of each type are different. A low degree of modification of particular groups of the enzyme is most likely to involve groups of type I, a moderate degree of modification involves groups of types I and II, while exhaustive modification can result also in the modification of groups of type III in the enzyme. After the modification of groups of type III in the protein, the entire system of intramolecular stabilising interactions breaks down and the destabilising effect arising as a consequence of the modification of these groups can therefore overlap the stabilising influence of the modification of groups of type II.

Analysis of the data in Table 1 shows that in the general case there is a possibility of three types of modification of the functional groups of the protein: (1) modification with a change in the charge in the aminoacid residues which alters the electrostatic interactions of the groups on or near the surface of the protein and its isoelectric point and can therefore change the conformation of the globule;[89] (2) modification with introduction of hydrophobic groups into the protein, which can have different effects on the properties of the latter depending on the location and nature of the hydrophobic group introduced, exerting the greatest influence on the conformation, the solubility, and the surface characteristics of the protein; (3) the introduction of hydrophilic groups into the protein molecule, which has little influence on its properties, since the surface of the protein globule is hydrophilic.

The above analysis of the problem of the stability of globular proteins and of the characteristics of the structure of t-proteins permits certain hypotheses concening the possibility of the stabilisation of enzymes as a result of their chemical modification: (1) the stability can increase on formation in the protein after modification of even a small

number of additional non-covalent linkages; (2) modification with introduction of charged groups can exert a great stabilising influence provided that the formation of additional salt bonds is possible; (3) the replacement of the amino-groups of Lys by arginine-like groups following the introduction of amide or guanidine groups should increase the stability of the protein; (4) other conditions being equal, imparting of hydrophobic properties to the protein molecule can hardly appreciably increase its stability. These features have been confirmed in practice, as will be shown below.

The main difficulty in the analysis of literature data is that of comparing the results obtained by different workers on different objects, because almost no systematic and comprehensive investigations of the influence of modification on the structure and stability of proteins are described in the literature. The authors have used different stability criteria, although, as already mentioned, only ΔG_{den} and, in the case of irreversible thermal inactivation, $\Delta G^{\neq}_{den}$, can serve as objective measures of stability. The equilibrium constant K_{den}, related to ΔG_{den}, can be conveniently used as a quantitative characteristic of the thermal denaturation process:

$$\ln K_{den} = -\frac{\Delta G_{den}}{RT},$$

while the rate constant k_{in}, related to $\Delta G^{\neq}_{den}$, can be used for irreversible thermal inactivation:[3]

$$\ln k_{in} = \ln \frac{k_B T}{h} - \frac{\Delta G^{\neq}_{den}}{RT},$$

where k_B is the Boltzmann constant.

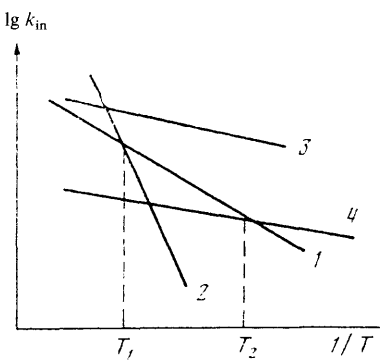


Figure 7. Hypothetical Arrhenius lg k_{in} relations for the native (line *1*) and modified or immobilised (lines *2–4*) enzymes; T_1 and T_2—isokinetic temperatures for the low-temperature (T_1) and high-temperature (T_2) stabilisation.[3]

When the thermal stabilities of the native and modified enzymes are compared, it is essential to compare the temperature variations of $\Delta G_{den}(K_{den})$ or $\Delta G^{\neq}_{den}(k_{in})$. The stabilisation effect θ^t at a given temperature is defined as the ratio of k_{in} for the native enzyme to k_{in} for the modified enzyme, i.e. $\theta^t = k_{in,nat}/k_{in,mod}$. If this ratio is greater than unity, then the modification stabilises the enzyme at a given temperature, while in the case where it is less than unity modification has a destabilising effect. The greater $\Delta G^{\neq}_{den}$, the more stable the enzyme (the smaller the value of k_{in}). The change of $\Delta G^{\neq}_{den}$ after the modification of the enzyme can be caused by the dominant alteration of the enthalpy term ($\Delta H^{\neq}$) or the entropy tern ($\Delta S^{\neq}$) in accordance with the equation

$$\Delta G^{\neq}_{den} = \Delta H^{\neq} - T\Delta S^{\neq}.$$

The quantity $\Delta H^{\neq}$ is determined from the experimental activation energy for the thermal inactivation process E_a: $\Delta H^{\neq} = E_a - RT$. When E_a for the thermal inactivation process is altered following the modification of the enzyme, one can observe two possible cases (Fig.7):[3,86]

(1) An increase of E_a (and $\Delta H^{\neq}$) for the modified enzyme. Depending on the scale in the change of $\Delta S^{\neq}$, the Arrhenius relations for K_{in} for the native and modified enzymes intersect outside or within the limits of the experimental temperature range (Fig.7, curves *1* and *2*). The modified enzyme is more stable than the native enzyme below the isokinetic temperature. The stabilisation effect increases with decrease of temperature. This is the case of the "low-temperature stabilisation" of the enzyme.

(2) A decrease of E_a (and $\Delta H^{\neq}$) after modification (Fig.7, curves *1* and *3*). The stabilisation effect can be observed only above the isokinetic temperature and is greater the higher the temperature at which it is considered. This is the case of the "high-temperature stabilisation".[3]

If $\Delta H^{\neq}$ changes little after modification, then the stabilisation (destabilisation) effect is due solely to the decrease or increase of $\Delta S^{\neq}$. Consequently, the study of the temperature variation of k_{in} makes it possible to discover the conditions under which the modified enzyme is more stable than the native enzyme and the extent to which this happens (and conversely). The knowledge of the temperature variation of k_{in} makes it possible to estimate objectively the enzyme stabilisation (or destabilisation) effects after the enzyme has been modified. The inadequate amount of information derivable from many literature stability data can be explained by the fact that they have been obtained at a single temperature.

1. Analysis of Experimental Data for the Influence of Chemical Modification on the Structure and Thermal Stability of Proteins and Enzymes

Studies of the influence of chemical modification by monofunctional agents are considered in this Section. We shall not deal with the results obtained on modification by bifunctional agents, because the effects of covalent intermolecular or intersubunit binding as well as the effect of the formation of intramolecular cross-links are superimposed on the single-point modification effects, which hinders an unambiguous interpretation of the results.

(a) The influence of the degree of modification on the structure and stability of proteins and enzymes. The modification of ~50% of the side residues frequently does not alter the conformation, the hydrodynamic properties, and the sedimentation constant of the protein (Table 1). The most accessible surface groups of type I are apparently modified in this case. For a number of proteins and enzymes (cytochrome *c*, horseradish peroxidase, and chymotrypsin), local changes in conformation are observed for a specific degree of modification indicating an increase of the number and energy of the intramolecular bonds.[29,108,109,116] At the same time, an increase of the stability of the macromolecules has been noted: the dominant increase of $\Delta H^{\neq}_{den}$ compared with $\Delta S^{\neq}_{den}$. In this case groups of type II were apparently modified. Table 1 shows that proteins and enzymes contain few groups of type II (from one to five). For high degrees of modification, involving internal groups which are masked

in the native conformation and which are involved in the main protein stabilising interactions, the conformation of the macromolecule changes sharply approaching that of the denatured macromolecule. The stability of the protein diminishes as a result of the dominant decrease of $\Delta H^{\neq}_{den}$ compared with that of $\Delta S^{\neq}_{den}$ (Table 1). Consequently, functional groups of type III are modified in this case.

Various acylating agents are used most frequently for modification (Table 1). Many workers assume *a priori* that only the NH_2 groups of Lys are modified and yet the SH groups of Cys and the OH of Tyr, Ser, Thr, and carbohydrate residues are also readily acylated[34,117,118] and a change in the properties of the acylated proteins can be caused by the modification of all the groups indicated and not only the amino-groups. When account is taken of this factor, the literature data might be interpreted somewhat differently. The influence of the degree of modification on their stability has been studied only for a small number of proteins and enzymes (Table 1). Some of these studies must be considered in greater detail.

Interesting results for the influence of the degree of modification on the structure and stability have been obtained for cytochrome *c*—a protein with a known tertiary structure. The stability of cytochrome *c* is determined by the stability of its conformation with a closed structure of the haem crevice[29,101] and is determined by two bonds: the salt bond between Lys (13) and Glu (90) "on top" of the crevice and the hydrogen bond between Lys (79) and the carbonyl residue (47) at the "bottom" of the crevice. The modification of Lys (13) results in a sharp broadening of the crevice and the destabilisation of the protein (k_{in} increases in the temperature range 25–60 °C). The modification of two Lys residues remote from the "bottom" and the "top" of the haem crevice does not influence the conformation and stability of the protein. The two NH_3^+ groups of Lys on the frontal surface of the molecule destabilise the latter as a consequence of electrostatic repulsion and the reversal of their charge therefore stabilises cytochrome *c* as a consequence of the diminution of the repulsion or the formation of new surface salt bonds. The modification of the three Lys residues located "on top" of the crevice in the region of the protein stabilising the Lys (13)–Glu (90) salt bond somewhat diminishes its stability as a consequence of the competition between the negatively charged carboxydinitrophenyl residues introduced and Glu (90) for Lys (13).[29]

With increase of the degree of modification of the amino-groups in bacterial α-amylase by *p*-nitrophenyl acetate to 10.5 groups at 75 °C, the thermal stability improves.[110] The temperature variations of k_{in} for α-amylases with different degrees of modification intersect in one point at 67 °C and have $E_a(\Delta H^{\neq})$ smaller than the native enzyme and to a greater extent the greater the degree of modification.[111] This means that, at temperatures below 67 °C, the thermal stability of the acetylated α-amylase is lower than that of the native enzyme and to a greater extent the higher the degree of modification. Above 67 °C the opposite relation between the thermal stability and the degree of modification is observed.[110] This is an example of the "high-temperature stabilisation". According to the authors,[111] the decrease of $\Delta H^{\neq}(\Delta S^{\neq})$ for the thermal inactivation process from 83 to 46 kcal mol^{-1} on modification of 11.5 Lys residues is due to a change in the conformation of the enzyme to give a partly uncoiled activated state.

We have shown that the "low-temperature stabilisation" of horseradish peroxidase is observed after the modification of Lys residues by trinitrobenzenesulphonic acid (TNBSA) or by oenanthic anhydride.[108] The Arrhenius plots for the $\lg k_{in}$ for the native enzyme and peroxidases with different numbers of modified Lys residues intersect, as for α-amylase, at the isokinetic point (75 °C). The modification of two amino-groups hardly alters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the thermal inactivation of the enzyme. For peroxidase with 3–4 modified groups, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are much greater than for the native enzyme and increase with increasing degree of modification (Fig.8). The stability of peroxidase modified in this way is many times greater than that of the native enzyme at all temperatures below 75 °C and the difference between their stabilities is greater the lower the denaturation temperature. For example, at 50 °C, the modified enzyme is ~100 times more stable than the native enzyme. The modification of all six Lys residues present in peroxidase diminishes $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for thermal inactivation and hence the thermal stability of the enzyme (Fig.8). Thus, we have been able to isolate three types of Lys residues in peroxidase in terms of their accessibility and role in the stabilisation of the globule: two residues on the surface of the enzyme, whose modification does not alter the thermal stability regardless of the nature of the modifying agent (groups of type I); two residues whose modification stabilises the enzyme and the stabilisation effect depends on the nature of the residues introduced (groups of type II); two residues located within the globule whose modification destabilises peroxidase (groups of type III). The increase of thermal stability after the modification of 3–4 Lys residues is correlated with the changes in the circular dichroism spectra of peroxidase indicating an increase of the strength of the haem-protein bond after modification.[108,109] This relation can be understood because the rate-limiting stage in the peroxidase thermal inactivation process is the dissociation of the haem–protein complex with subsequent denaturation and aggregation of the apoprotein.

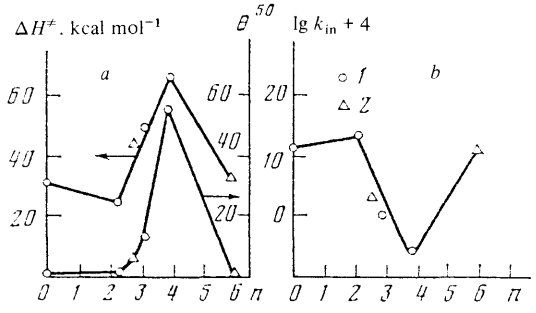


Figure 8. The influence of the number *n* of modified ε-NH_2 Lys groups in peroxidase on $\Delta H^{\neq}$ for irreversible thermal inactivation and on the stabilisation effect ($\theta = k_{in,nat}/k_{in,mod}$) at 50 °C (*a*) and on $\lg k_{in}$ at 50 °C (*b*) (pH 7.0); the peroxidase was modified with oenanthic anhydride (*1*) and TNBS (line *2*).[121]

We have shown[34] that the acetylation of peroxidase entails the modification at 0–22 °C, together with that of the Lys residues, also of the surface OH groups (up to 30 groups) of Tyr, Ser, Thr, and the carbohydrate component of the enzyme, which belong to type I: regardless of its extent, their modification does not influence the thermal stability of the enzyme over the entire experimental temperature range (60–80 °C).[34] With increase of temperature (40 °C), the internal groups are acylated in addition to the three surface NH_2 and OH groups (groups of type I and II): one OH group of Tyr and the OH groups of other residues (groups of

type III). The stability of peroxidase then diminishes by a factor of ~8 at 50 °C compared with the native protein and by a factor of 100 compared with the peroxidase having three acylated amino-groups. The observed destabilisation effect is due exclusively to the modification of the internal OH groups of the enzyme.[34] After the removal of the modification of these groups with the aid of hydroxylamine, the thermal stability of the enzyme again rises sharply (by a factor of 100), i.e. becomes the same as that of the peroxidase with three modified amino-groups (Fig.8). The one internal OH group of Tyr is particularly important for the stability of native peroxidase.

The virtually complete modification of the amino-groups of α-chymotrypsin by succinic anhydride causes little alteration to the structure of the molecule (as can be seen from absorption and circular dichroism spectra) and to its kinetic properties.[115] Following the alkylation of 60% of its amino-group by acrolein and succinylation, the thermal stability of chymotrypsin increases insignificantly. For a degree of modification of 60–95%, the thermal stability of the enzyme increases sharply (by factors of 20 and 100 respectively) and after the complete substitution of the amino-groups it falls to the level for the main enzyme.[116] The authors introduced the concept that the enzyme contains several "key" groups whose modification sharply increases its thermal stability.

Thus the structure and stability of proteins and enzymes depend significantly on the degree of modification of their functional groups. For a large number of other proteins, the dependence of the thermal stability on the degree of modification also passes through a maximum (Table 1): for ribonuclease,[102,105,106] glucoamylase[107] and guanidinated lactate dehydrogenase.[113,114] Groups of types I, II, and III can be detected in virtually every protein.

Local chemical modification. Like point mutations, such modification makes it possible to discover the role of individual aminoacid residues in the stabilisation of the native conformation of the protein. On transamination, the N-terminal amino-group of the main pancreatic inhibitor of trypsin is replaced by the keto-group, which entails the removal of one salt or hydrogen bond. In the presence of 6 M guanidine hydrochloride, T_{den} diminishes after modification from 75° to 68 °C, while at pH 1.0 neither the native nor the modified protein are denatured up to 82 °C. Consequently, the $NH_3^+ \ldots COO^-$ salt bond stabilises the inhibitor at neutral pH but not at acid pH, where the COOH group is protonated. The authors believe that one salt bond with an energy of ~1 kcal mol^{-1} can play an important role in the stabilisation of the native conformation of the inhibitor.[122]

Three other local modifications have also been carried out in the pancreatic inhibitor: (1) one S–S bond was reduced; (2) one Lys–Ala peptide bond was cleaved; (3) the Ala (16) and Arg (17) residues were removed from the active centre. Only local changes were then observed in the conformation near the region of the modifications, while the overall conformations of the modified molecules corresponded to the structure of the native inhibitor. On the other hand, the stability of the globular conformation of the modified protein diminished appreciably and the exchange of the internal amide protons of the protein with the solvent became faster.[123]

After the reduction of the S(14)–S(38) bond [compound (I)], the SH groups formed in the inhibitor were modified by means of charged residues: with iodo acetamide [a neutral group was introduced—compound (II)], with iodoacetic acid [a negatively charged group was introduced—compound (III)]; with ethyleneimine [a positively charged group was introduced—compound (IV)]. The three-dimensional structures of the reduced compound (I) and the three modified proteins proved to be almost identical, but T_{den} was altered: T_{den} = 76 °C for compounds (I) and (II), T_{den} = 79 °C for compound (III), and T_{den} = 70 °C for compound (IV). Thus the maximum stability of the reduced inhibitor was attained when the SH groups were modified with negatively charged groups, because the S–S bond cleaved is located in the positively charged cluster made up of Lys and Arg residues and the groups introduced form with the latter new ion pairs which stabilise the protein. At the same time, the introduction of a positively charged group destabilised the inhibitor for the same reason.[124]

The local chemical modification clearly demonstrates the fact that the modification of the groups involved in protein stabilising interactions diminishes the stability of the protein. An increase of the stability of the protein after modification is observed only on formation of new additional bonds, particularly salt bonds.

(b) The influence of the nature of the residues introduced on modification. The nature of the modifying agent has an appreciable influence on the stability of the macromolecules, particularly in the modification of groups of type II. The possible instances of modification can be divided into several groups: (1) modification with retention of the charge of the modified groups; (2) modification of uncharged residues by uncharged agents; (3) modification involving a change in the charge of the modified groups; (4) modification with change in the hydrophobic properties of the residues introduced.

Modification with retention of the charge of the modified groups. Mainly three modification reactions are used to modify the Lys residues with retention of their positive charge. Amidination with the aid of iminoesters:

$$E\text{—}NH_3^+ + R'\text{—}O\text{—}C(=NH_2^+)R \rightarrow E\text{—}NH\text{—}C(=NH_2^+)R \quad (1)$$

Guanidination with *O*-methylisourea:

$$E\text{—}NH_3^+ + CH_3O\text{—}C(=NH)NH_2 \rightarrow E\text{—}NH\text{—}C(=NH_2^+)NH_2 \quad (2)$$

Modification with aldehydes followed by reduction of the Schiff bases formed:

$$E\text{—}NH_3^+ + RCHO \rightarrow E\text{—}N{=}CH\text{—}R \xrightarrow{NaBH_4} E\text{—}NH_2^+\text{—}CH_2\text{—}R \quad (3)$$

In the first two cases arginine-like groups are introduced into the protein and the p*K* of the Lys residues increases from 10.5 to 12.5 after modification.[125] In the third case the primary amino-group is replaced by a secondary amino-group whose p*K* is somewhat reduced.

We may recall that an increased content of Arg residues compared with Lys residues is characteristic of many t-enzymes (Section II). For example, for less stable proteinases (pig chymotrypsin and trypsin), the Arg : Lys ratios are 4 : 14 and 2 : 14 respectively, while for the more stable enzyme elastase the ratio is 12 : 3.[126] It is therefore logical to expect an increase of the stability of the proteins and enzymes after the guanidination of the Lys residues. Indeed, after the modification of the Lys residues in seven proteins of six different classes with *O*-methylisourea, their stability increases (ΔG for the internal and external tritium exchange increases). This is due to the decrease of the conformational mobility of the local segments of the protein structure.[126]

The guanidination of 15 Lys residues in lactate dehydrogenase does not alter appreciably the protein conformation but greatly increases the thermal stability of the enzyme, which the authors believe to be caused by the formation of the $COO^- \ldots NH_2{=}C(NH_2)E$ salt linkages both within the subunits and between them.[113] A somewhat smaller stabilisation

effect has been observed on acetamidination of the same enzyme.[127] On the other hand, the modification of lactate dehydrogenase with formaldehyde followed by the reduction of the azomethine bonds decreased its thermal stability and even induced partial dissociation of the tetramer.[128] Thus the important role of salt bonds in the stabilisation of the protein has been demonstrated in relation to lactate dehydrogenase: the greater the charge on the modified Lys residues, the stronger the electrostatic interactions stabilising the macromolecule.

The acetamidination of a number of other enzymes (thermophilic glutamine synthetase[129] and peroxidase[34]) also increased their thermal stability and only local changes in the protein conformation were then observed. The increase of the stability of trypsin after the acetamidination of Lys was explained, in particular, by the decrease of its autolysis.[130]

On the other hand, the excess guanidination of proteins by converting their COOH groups into amino-groups with subsequent modification using *O*-methylisourea should apparently lead to their destabilisation as a consequence of the electrostatic repulsion of a large number of positively charged groups, as has been shown for chymotrypsinogen.[131]

Thus the amidination and guanidination of proteins, in which their physicochemical properties are fully retained, can serve as a simple and convenient general method for their stabilisation. The stabilisation mechanism apparently consists in the fact that the arginine-like residues are more hydrophilic than Lys, which reduces the possibility of finding them within the hydrophobic nucleus of the molecule compared with Lys. The arginine-like residues increase the rigidity of the protein globule and, having a higher p*K* than Lys, form stronger salt bonds in the protein.[126]

Less unambiguous results have been obtained in the study of the stability of proteins in which the Lys residues were subjected to the reductive alkylation [reaction (3)].

Thus modification of aminogroups with propionaldehyde or glutaraldehyde decreased the thermal stability of chymotrypsin at 60 °C by a factor of 1.5–3 depending on the pH, while modification with acrolein increased its thermal stability by a factor of 100 under the same conditions.[116,132] Modification with glutaraldehyde decreased the thermal stability of trypsin[133] but increased that of glycogen phosphorylase b [134] and β-glucosidase.[135] Unfortunately, the data for the stability of proteins modified by glutaraldehyde are difficult to interpret owing to the complexity and ambiguity of the processes occurring during modification.[88]

In the general case one should note that the positive charge on the amino-groups of proteins is retained during their alkylation, but hydrophobic residues are introduced whose presence on the surface of the macromolecule is frequently inconvenient. After modification, the capacity of the amino-group for the formation of salt bonds also diminishes. These are apparently in fact the main causes of the decrease of the thermal stability of the majority of proteins and enzymes after reductive alkylation.

Modification of the uncharged residues with uncharged agents. In this case one is dealing primarily with the modification of polar OH groups in the Ser, Thr, and Try residues, as well as the residues of aromatic aminoacids and the carbohydrate groups in glycoproteins. The main reactions used for this purpose were (1) acylation with monocarboxylic acid anhydrides, (2) oxidation of carbohydrate residues, and (3) nitration or iodination of Tyr or Trp residues.

The acylation of up to 30 surface OH groups by monocarboxylic acid anhydrides in horseradish peroxidase does not influence its thermal stability.[34]

Many plant proteins and enzymes contain covalently bound carbohydrate residues which form a polar "coat" round the macromolecules protecting them from proteolysis and stabilising their tertiary structure.[136] The oxidation of carbohydrate residues by sodium periodate or their removal with the aid of enzymes therefore as a rule diminishes the thermal stability of glycoproteins: invertase,[136] cellulase from thermophilic fungi,[77] t-glucosidase from *Mucor miehei* UN-10,[137] and catalase.[138] As was to be expected, the destabilisation effect depends on the degree of modification of the carbohydrate residues. For example, the deglycosylation of 20% of the carbohydrate residues in the catalase of *A.niger* does not influence the stability of the enzyme while after the oxidation of 40% of the carbohydrate residues, $T_{1/2}$† diminishes after 10 min from 75° to 72 °C.[138] The destabilisation effect for glucose oxidase, 50% of the carbohydrate residues of which are oxidised by periodate, is observed only in the presence of denaturing agents: sodium dodecylsulphate or urea. In this case $\Delta H^{\neq}$ for the enzyme diminishes by a factor of 1.3.[139,140] In certain cases, for example, for horseradish peroxidase, the oxidation of carbohydrate residues does not alter the thermal stability of the enzyme.[141]

On the other hand, the covalent addition of polysaccharides to proteins and enzymes as a rule increases their thermal and pH stability as well as their resistance to proteolysis.[2,7] The cause of the universal stabilising action of polyols bound covalently to the protein has become clear in the study of the influence of added sucrose and other polyols on the stability of proteins in solution. It has been established that sugar solutions are a less favourable solvent than water for aromatic and aliphatic aminoacids.[142] Sugars increase the surface tension of water and the degree of structure formation in it near the surface of aminoacid residues of the protein to a greater extent the larger the number of equatorial OH groups in their molecule. This makes the uncoiled (denatured) conformation of the macromolecule thermodynamically less favourable and shifts the equilibrium between the native and denatured protein towards the former, which increases ΔG_{den}.[143] Thus the stabilisation of proteins in sugar solutions or after the covalent binding of sugars is due to the enhancement of the intraglobular hydrophobic interactions. The stabilising action of added glycerol involves a different mechanism: glycerol reduces the surface tension of water and interacts mainly with the polar groups on the surface of the protein molecule.[143] An increase of the glycerol concentration in the protein solution diminishes $\Delta H^{\neq}_{den}$ (and $\Delta S^{\neq}_{den}$) for cytochrome P-450.[144,145]

The nitration of thermolysin with tetranitromethane decreases by a factor of two its activity and thermal stability, while the percentage content of the α-helix remains unaltered. It has been shown that the Tyr and Trp residues are modified in the enzyme, being probably present in the hydrophobic region of the molecule. For this reason, their modification following the introduction of the nitro-group destabilises the enzyme.[146]

Modification with alteration of the charge on the modified groups. The change in the charge (its removal or reversal) of the functional groups of the protein takes pldce on modification of the charged Lys, Arg, Glu, and Asp residues and on acylation of the polar Ser, Tyr, and Thr residues with dicarboxylic acid anhydrides. The modification which alters the sign of the modified group makes it possible to discover the influence of both the overall charge of the molecule and of the local electrostatic interaction on the structure and stability of the protein. The charged and polar residues are located as a rule on the surface of the protein globule and can be involved in local interactions, stabilising or

† $T_{1/2}$ is the temperature at which 50% of the enzyme is inactivated during a specific selected time interval.

destabilising the native conformation of the molecule. Since salt bonds both within the globule and near the surface of the macromolecule play a significant role in its stabilisation, their formation or rupture as a result of modification should be markedly reflected in the stability. The majority of studies of the influence of modification on the stability of proteins and enzymes have been devoted to the acylation of their amino-groups, whose positive charge is removed or reversed. Such modification can also involve the SH and OH groups.[118]

One of the first studies dealt with the stability of acylated trypsin.[147–149] Admittedly, the data obtained are not easy to interpret unambiguously since the blocking of the Lys amino-groups in trypsin diminishes autolysis apart from anything else, which increases the stability of the enzyme.[147] For example, acetyltrypsin is more stable than the native enzyme in an alkaline medium at 25 °C, but is less stable in an acid medium. Its thermal stability is also lower than that of the native enzyme. Modification of trypsin by various monocarboxylic and dicarboxylic anhydrides showed that, for the same degree of modification of the amino-groups at 100 °C and pH 5.5, the monocarboxylic acid derivatives are the least stable. Their stability increases in the sequence acetyltrypsin, propionyltrypsin, butyryltrypsin, diethylacetyltrypsin, phthalyltrypsin << β-sulphopropionyltrypsin < itaconyltrypsin < native trypsin < succinyltrypsin < citraconyltrypsin.[148,150] Succinyltrypsin is more stable than the native enzyme also at pH > 5. According to the authors, the electrostatic repulsion of the equally charged COO^- groups introduced is a factor stabilising the enzyme. On the other hand, acylation has little influence on the denaturation of trypsin by urea.[149] Thus, the removal of the charge from the amino-group diminishes the thermal stability of the protein, while its replacement by a negative charge increases somewhat the thermal stability.

The acetylation of alkaline phosphatase increases its thermal stability at 30 °C and at pH from 4.0 to 11.0. The authors believe that the protecting effect of acetylation and alkaline pH is common to many proteins, which is surprising in view of the fact that acetylation greatly increases the overall negative charge of the enzyme molecule, which is in any case high at alkaline pH.[151] Acylation increases the stability of thermolysin,[152] but diminishes the thermal stability of subtilisin and ferredoxin.[153,154]

Invertase from baker's yeast has been modified by citraconic anhydride, acetaminoester, and carbodiimide in the presence of ethylenediamine. The reversal of the sign of the charge on the NH_3^+ and COO^- groups significantly destabilised the enzyme (65 °C), while modification with retention of the positive charge on the amino-groups did not affect the stability. The authors conclude that the native structure of invertase is stabilised by the $NH_3^+ \ldots COO^-$ salt bonds whose rupture on modification of either amino- or carboxy-groups destabilises the enzyme.[155]

For the same degree of modification of the NH_2 groups of α-chymotrypsin, the greatest stabilising effect was shown by the modification of the enzyme with acrolein (the positive charge is retained).[116,153] The weakest stabilisation was observed on acylation with acetic, succinic, and citraconic anhydrides, possibly because, in contrast to the first modification, functional groups other than the NH_2 group were acylated in the enzyme and their modification might have destabilised the latter.

The thermal stability of pepsin increases at 30 °C by a factor of 10–20 (depending on the excess of the nucleophile employed) when its COOH groups are modified with the aid of carbodiimide and methyl glycinate. The stabilisation of the enzyme is due to the decrease of the overall negative charge after modification, because native pepsin is rapidly denatured at pH 7.0 as a consequence of the electrostatic repulsion of the large number of negatively charged COOH groups.[156]

The removal of the charge, as a result of the modification, from the lysine (13) residue, which forms the main salt bond maintaining the closed structure of the haem crevice in cytochrome *c*, fully destabilises the protein. On the other hand, modification involving the removal of the charge from Lys residues destabilising the native protein results in a further closure of the haem crevice.[29]

For each degree of modification of the amino-groups of pig heart lactate dehydrogenase, the neutralisation of the positive charge after their modification with methyl 4-hydroxy-3-nitrobenzimidate (the aminophenoxide form) (Table 1) as well as acetylation greatly destabilise the enzyme. On the other hand, the aminophenol form of the modified amino-groups (the positive charge is retained) increases the stability of the enzyme like its acetamidination and guanidination.[114]

The removal of the positive charge from virtually all the amino-groups of malate dehydrogenase after acetylation or modification with methyl 4-hydroxy-3-nitrobenzimidate diminishes $T_{1/2}$ for the enzyme (after 20 min) by 16–17° and 7 °C respectively. The decrease of stability is apparently caused by the breakdown of intersubunit interactions in which the Lys residues are involved.[157]

The influence of the charge on the amino-group on the thermal stability of horseradish peroxidase has been determined by comparing the stabilities of the enzyme whose four amino-groups have been modified with acetimidate and butyric, succinic, and maleic anhydrides.[34,158] Whilst retaining the positive charge on the amino-group, acetamidination adds the small methyl residue and increases the length of the "foot" at the positive charge by ~1.5 Å. After modification with butyric anhydride, the positive charge of the amino-group disappears, while modification with succinic and maleic anhydrides results in the introduction of a negative charge. All three types of residues introduced have a similar structure. After acetamidination, $\Delta H^{\neq}$ for the thermal inactivation of peroxidase increases and hence the thermal stability at temperatures below 75 °C increases somewhat; it increases by a factor of 2.5 after modification with butyric anhydride and by a factor of 3 after modification with succinic and maleic anhydrides. This can be explained by the decrease of the local and not the total positive charge of the macromolecule. It may be that the two amino-groups of the peroxidase are located in the hydrophobic cavity or in a positively charged cluster of groups and destabilise the native structure of the enzyme. Their modification with removal of the positive charge or the introduction of a negative charge promotes the formation of additional salt bonds in the molecule, which increase the strength of the haem–protein bond, i.e. the thermal stability of the enzyme. Even a slight increase of the length of the "foot" at the positive charge of the amino-group after acetamidination increases somewhat the thermal stability of peroxidase. On the other hand, the appearance of a negative charge on a large number of surface OH groups of peroxidase on succinylation does not affect the thermal stability of the enzyme.[34]

Thus data for the modification of the functional groups involving a change in the charge demonstrate the different roles of the charged aminoacid residues in the stabilisation of the native structure of enzymes. In trypsin, subtilisin, invertase, and lactate and malate dehydrogenases, the amino-groups of the Lys residues are involved in the formation of intramolecular salt bonds or in maintaining the three-dimensional structure of the native enzyme. The removal of the charge from these groups destabilises the enzymes. On the other hand, in a number of enzymes (peroxidase,

cytochrome *c*, chymotrypsin, pepsin, etc., amino- or carboxy-groups destabilising the native protein as a consequence of unfavourable electrostatic interactions have been discovered. Their modification, involving a change in the charge, makes it possible to achieve large stabilisation effects (by factors up to 100 for peroxidase and chymotrypsin).

The influence of the hydrophobic nature of the residues introduced. For the same degree of modification and using modifying agents with similar chemical structures, the influence of the hydrophobic properties of the residues introduced on the stability of proteins and enzymes has been analysed in a number of investigations. In order to elucidate this influence in a "pure" form, it is more correct to compare with one another the properties of members of a series of modified enzymes which differ only by the length of the hydrocarbon residues incorporated in them and not the properties of the native and modified enzymes. Although the number of studies devoted to this question is small, they make it possible to elucidate the overall dependence of the thermal stability of enzymes on the hydrophobic properties of the groups introduced, which is represented by a curve with a maximum (Fig.9). Such relations have been obtained for phosphorylase *b*,[159] α-amylase,[110] horseradish peroxidase,[86, 108] and thermolysin,[152] the accessible amino-groups of which were alkylated or acylated by a series of agents with different hydrophobic properties. In all cases an increase of the thermal stability of the enzymes was observed after their modification [derivatives of the type $E(NHR)_n$ or $E(NHCOR)_n$, where n is constant for each enzyme and R varies].

In phosphorylase *b* ~10% of the Lys residues were modified by aldehydes derived from monocarboxylic acids (from C_2 to C_7) and the azomethine bonds were reduced with $NaBH_4$ (the positive charge on the amino-group is retained under these conditions). Thermal stability at 0° and 50 °C increased with increase of the length of the hydrocarbon residue R in a series of derivatives $E(NHR)_n$ from C_2 to C_5 and then diminished (Fig.9). When the polar glyceraldehyde was used, the stabilising effect was hardly observed.[159]

For bacterial α-amylase, whose amino-groups were modified by the *p*-nitrophenyl esters of monocarboxylic acids (C_1, C_7, and C_{15}), the greatest stabilisation effect was observed after the introduction of the CH_3 group, while for the C_7 and C_{15} derivatives the stability diminished with increase of the length of the hydrocarbon residue.[110] Since data for other derivatives in this series are lacking, it is not known what should be the length of the hydrocarbon residue to give the optimum stabilisation. Possibly it is in the range from C_1 to C_7.

In a series of preparations of peroxidase acylated by monocarboxylic acid anhydrides [the $E(NHCOR)_4$ derivatives, where $R = C_nH_{2n+1}$] the thermal stability $\Delta H^{\neq}_{den}$ increases with increase of the size of the hydrocarbon residue R introduced from C_1 to C_3, while on further increase of R from C_3 to C_6 $\Delta H^{\neq}_{den}$ diminishes (Fig.9). Each succeeding member of the series differs from the preceding one only by the addition of four CH_2 groups. The increment $\Delta(\Delta H^{\neq}_{den})$ per methylene group is 1.5–2 kcal mol^{-1}.[86,108]

The hydrophobic properties of the residues introduced can be varied not only by altering their size but also be replacing the hydrophilic groups in R by hydrophobic groups. For example, the seven accessible amino-groups of thermolysin have been modified by a series of derivatives of normal carboxylic acids, the $[E(NHCOR)_7$ derivatives, where $R = C_{n+8}H_{2n+17}.O_{5-n}]$. The enhancement of the hydrophobic properties in this series was achieved by replacing the ester group by the methylene group. The methylene group enhances the hydrophobic properties of the aminoacid side residue by ~0.7 kcal mol^{-1}, while the ester group diminishes it by ~0.7 kcal mol^{-1}. Thus the replacement of one ester group by the methylene group enhances the hydrophobic properties of the residue by ~1.4 kcal mol^{-1}. The hydrophobic properties of the residues become more pronounced when n is varied from 1 to 5. For n = 4 and 5, insoluble and relatively inactive derivatives are obtained and these were not investigated further. The thermal stability of other derivatives with n = 1–3 varied at 80° and 90 °C as shown in Fig.9, i.e. it passed through a maximum at n = 1.[152]

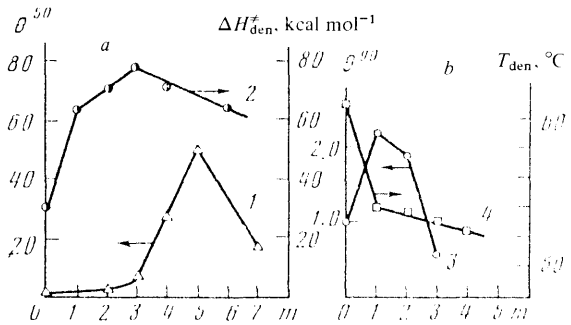


Figure 9. Dependence of the stability of enzymes on the hydrophobic properties of the residues introduced on modification; n is the number of C atoms in the residue for modified derivatives of type $ENHC_nH_{2n+1}$ for phosphorylase *b* (line *1a*),[159] $E(NHCOC_nH_{2n+1})_4$ for horseradish peroxidase (line *2a*),[86,108] $E(NHCOC_{n+8}H_{2n+17}O_{5-n})_7$ for thermolysin (line *3b*)[152] and $E(NHCOC_nH_{2n+1})_{12}$ for ribonuclease (line *4b*);[162] the stabilisation effect ($\theta = k_{in,nat}/k_{in,mod}$) at 50 °C (line *1a*) and 90 °C (line *3b*), the enthalpy of the denaturation process $\Delta H^{\neq}_{den}$ (line *2a*), and the average denaturation temperature T_{den} (line *4b*) have been used as measures of stability.

There is no doubt that the hydrophilic nature of the surface of enzymes is important for their solubility and for the manifestation of their catalytic activity in aqueous solutions. In all the cases considered, the greatest stabilisation of proteins is attained for a definite and comparatively small length of the hydrocarbon residue R: at C_3 for peroxidase and at C_5 for phosphorylase (Fig.9). The interaction of the hydrocarbon residues introduced, having the optimum length for each enzyme, with the nearest hydrophobic groups of the enzyme leads to the greatest stabilisation of the tertiary structure of the protein. On the other hand, when the size of R begins to exceed the size of the hydrophobic cavity in the enzyme molecule, the partial exposure of the R residue to the solution is thermodynamically unfavourable and results in a diminuation of stabilisation effects ($\Delta H^{\neq}_{den}$ decreases) and in certain cases leads to destabilisation. Analogous stabilisation effects for different proteins have been noted when the latter solubilised small amounts of hydrocarbons.[160,161] The dependence of ΔH for thermal denaturation of proteins in the presence of hydrocarbons also passes through a maximum and the increment $\Delta(\Delta H)$ per CH_2 group of the solubilised hydrocarbon is ~2 kcal mol^{-1}.

The dependence of the thermal stability on the hydrophobic properties of the residues introduced passes through a maximum i.e. the introduction of hydrophobic residues of specific dimensions into the protein can stabilise the latter only when the modification does not by itself diminish the stability of the

enzyme (or increases it). In those cases where the modification destabilises the enzyme, an increase in the length of the hydrophobic residues leads to a progressive albeit not very great diminution of the stability of the macromolecule. For example, the thermal stability of ribonuclease modified with different succinimides [the $E(NHCOR)_{11}$ derivatives, where $R = C_nH_{2n+1}$] decreases sharply when the C_1 derivative is used. The increase in the size of the residue R from C_1 to C_4 entails only a slight further decrease of the thermal stability of the enzyme (Fig.9). According to the authors, the destabilisation of the enzyme after modification is similar to the denaturation of ribonuclease by alcohols.[162]

The introduction of very bulky hydrophobic residues decreases sharply the stability of the enzyme in all cases regardless of whether the given modification itself stabilises or destabilises the enzyme. Despite the fact that acetamidination of lactate dehydrogenase stabilises the enzyme,[127] when a very bulky hydrophobic agent is employed, namely methyl *N*-(2,4-dinitrophenyl)-ε-aminocaproimidate, the thermal stability of the modified enzyme becomes smaller than that of the native enzyme. This is due to the marked enhancement of the hydrophobic properties of the enzyme globule and the rupture of the bonds between the Lys residues and other residues, which have a favourable effect on the stability, as a consequence of the introduction of large and bulky substituents despite their positive charge.[163] Thus the introduction of large hydrophobic residues can abolish the stabilising effect of the modification.

The observed change in the thermal stability of enzymes after modification is not always associated with the influence of the hydrophobic properties of the residues introduced. For example, the acylation of α-amylase by various *N*-hydroxysuccinimides and 1-hydroxybenzotriazole increases the thermal stability of the enzyme at 60 °C in the sequence native < α-amylase ($E - NH_2$) ≤ dimethylcarbamoylated α-amylase [$E - NHCON(CH_3)_2$], ethoxyformylated α-amylase ($E - NHCOOC_2H_5$) < formylated α-amylase ($E - NHCHO$) < acetylated α-amylase ($E - NHCOCH_3$) < dimethylpropanoylated α-amylase [$E - NHCOC(CH_3)_3$]. The increase of thermal stability in this sequence is correlated with the weakening of the electron-donating capacity of the amide nitrogen and not with the change in the hydrophobic properties of the residue introduced.[164]

In conclusion one should note that the "pure" contribution of the hydrophobic properties of the residues introduced to the observed stabilisation–destabilisation effect for the modified enzyme is extremely small compared with the effects of the local or overall changes in the charge of the molecule. For example, the acetylation of the four amino-groups of peroxidase increases $\Delta H^{\neq}$ for thermal inactivation by a factor of two (from 30 to 65 kcal mol^{-1}), while the additional contribution to the stability (to the increase of $\Delta H^{\neq}$) by the four CH_2 groups introduced does not exceed 6–8 kcal mol^{-1}.

2. Physicochemical Characteristics of the Change in the Stability of Enzymes after Their Chemical Modification and Immobilisation

The results in the previous Section clearly demonstrate that the chemical modification of the functional groups of enzymes not involved directly in the active centre by monofunctional agents can exert a strong influence on their structure and stability. The studies considered confirm the hypothesis of the existence in proteins and enzymes of three types of functional groups whose modification has different effects on their structure and stability.

The change in the thermal stability of enzymes as a result of their chemical modification is a consequence of local or overall changes in the three-dimensional structure of the protein—in the conformational mobility of individual fragments of the polypeptide chain. Despite the considerable alteration of the stability of the protein, the variations in its structure can frequently be so small that they cannot always be detected by analysing the absorption, fluorescence, or circular dichroism spectra.[127,129,165,166] The stability of proteins is therefore the most sensitive test for any change in their structure.[7,86]

The relation between the changes in the structure and thermal stability after chemical modification and the contributions of different types of groups in the protein have been clearly traced only for several enzymes, for example, for horseradish peroxidase.[34,86,108,109] Modification of groups of type I (up to 30 surface OH groups and two ε-NH_2 Lys groups) does not affect the structure and stability of the peroxidase regardless of the degree of modification. The modification of the other two ε-NH_2 Lys groups (groups of type II) with removal of the positive charge diminishes the conformational mobility of the protein in the haem-binding region, which is reflected in the circular dichroism spectra of the peroxidase. As a consequence of this, there is an appreciable increase of the stability of the enzyme. Finally, the modification of the internal OH and ε-NH_2 groups (groups of type III) reduces the intensity of the haem and aromatic aminoacid bands in the circular dichroism spectra, which indicates a weakening of the heam–protein bond and the approach of the structure of the enzyme to that which obtains after thermal denaturation. The thermal stability of such an enzyme is lower than that of the native enzyme.[108]

Analysis of the literature data shows that, as in the case of the proteins and enzymes from thermophilic sources (Section II), the main cause of the increase of the stability of the modified enzyme is the formation of additional bonds (salt and hydrogen bonds) within and on the surface of the molecule, the enhancement of the hydrophobic interactions in the protein, and also the strengthening of the bonds between the protein and the prosthetic groups, metal ions, etc.

Analysis of the temperature variations of k_{in} for the native and modified (including immobilised) enzymes shows that the stabilisation effect varies with temperature. The term "stabilisation" is significant only for a specific temperature range. "Absolute stabilisation", i.e. the case where the ratio of the constants k_{in} for the native and immobilised enzymes is the same over a fairly long temperature range, is hardly possible. It will be possible only when the $\Delta H^{\neq}_{den}$ for the native and modified enzymes are the same and $\Delta S^{\neq}_{den}$ for the modified enzyme is lower than for the native enzyme by an appreciable amount. However, in all cases known from the literature ΔH_{den} and ΔS_{den} (or $\Delta H^{\neq}_{den}$ and ΔS_{den}) for the enzyme thermal denaturation process vary in parallel after the chemical modification or immobilisation of the enzymes. This is apparently to be explained by the existence of a compensation effect for protein systems in solution, which is most likely to be determined by the properties of water.[167] This effect consists in the fact that, despite the large changes in ΔH_{den} (or $\Delta H^{\neq}_{den}$), the values of ΔG_{den} (or $\Delta G^{\neq}_{den}$) change little in most cases after the chemical modification or immobilisation of enzymes owing to the compensating effect of the entropy term $T\Delta S_{den}$. ΔG_{den} increases either because ΔH_{den} increases more than ΔS_{den} or because ΔS_{den} decreases more than does ΔH_{den}.

Fig.10 presents the experimental compensation relation between $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ for the thermal inactivation of a series of native and modified enzymes. The relation between $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ indicates the existing limits of variation of

these parameters as the nature of the modifying agent (or the carrier for immobilised enzymes) is altered or for different degrees of modification. All the points on the compensation relation lying to the left of those corresponding to the native enzymes correspond to preparations of the modified or immobilised enzymes for which $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ are smaller than for the native enzyme. Such preparations are more stable than the native enzyme above the isokinetic temperature ("high-temperature stabilisation"). All the preparations the points for which lie to the right of the point corresponding to the native enzyme have higher values of $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ than the native enzyme. These compounds are more stable than the native enzyme below the isokinetic temperature ("low-temperature stabilisation"). If the isokinetic temperatures are similar for different derivatives of the enzyme, then the modified enzymes are more stable below the isokinetic temperature the higher their values of $\Delta H^{\neq}_{den}$.

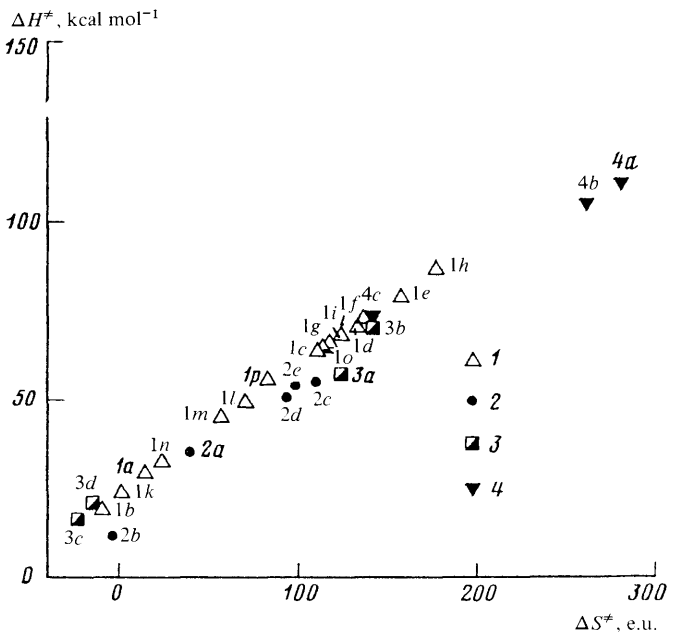


Figure 10. Compensation relation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the thermal inactivation of soluble (native and modified) and immobilised enzymes: 1) horseradish peroxidase: native (*a*), immobilised in polyacrylamide gel (*b*), modified (four NH_2 groups) with acetic (*c*), propionic (*d*), butyric (*e*), valeric (*f*), oenanthic (*g*), succinic (*h*), and maleic (*i*) anhydrides, modified with oenanthic anhydride [*k*) two NH_2 groups; *l*) three NH_2 groups] and trinitrobenzenesulphonic acid [*m*) three NH_2 groups; *n*) six NH_2 groups] and peroxidase–albumin conjugates [*o*) fraction I; *p*) fraction II]; 2) glow-worm luciferase: native (*a*), immobilised on ultragel (*b*), ultradex (*c*), cellophane (*d*), and Sepharose (*e*) and activated with bromocyanogen; 3) α-chymotrypsin: native (*a*), soluble conjugates with dextran (*b*), and sodium alginate (*c*), and immobilised on KM-cellulose (*d*); 4) β-galactosidase: native (*a*), and modified with a dye (*b*) and then sorbed on DEAE-Sephadex (*c*) according to different literature data.[39, 86,108,158,168,169,172,175,178]

Since the native and modified (immobilised) enzymes have different temperature variations of k_{in} (K_{den}), in the general case there is always a temperature range where the native enzyme is more stable and a range where the modified or immobilised enzyme is more stable (Fig.7). As the isokinetic point is approached, the difference between the stabilities of the native and modified enzyme diminishes, while under conditions remote from this point it increases.

Studies involving the comparison of the kinetic and thermodynamic parameters of the thermal inactivation of native and modified proteins and enzymes have shown that in many cases these parameters vary in parallel.[20,39,168] The increase or decrease of $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ for the thermal inactivation of enzymes after their chemical modification or immobilisation can be accounted for by a change in their thermodynamic stability and hence by a change in the relative contributions of various factors which determine the thermodynamic stability of the protein globule of the enzyme in solution.

Stabilisation of enzymes in solution after the chemical modification of their functional groups. Such stabilisation is caused as a rule by the increase of $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ for thermal inactivation. This is "low-temperature stabilisation" of enzymes below the isokinetic temperature (Fig.7, curves *1* and *2*), which is as a rule above 50 °C. Chemical modification of enzymes leading to an enhancement of the intramolecular interactions in the globule increases ΔG_{den} for the modified enzyme compared with the native enzyme, whereupon we have $\Delta G_{den,mod} - \Delta G_{den,nat} < 0$. The formation of additional intramolecular bonds on modification increases ΔH_{den}, while the introduction of additional residues increases ΔS_{den} (mainly as a result of an increase in conformational entropy). The greater the amount by which the increase of ΔH_{den} predominates over that of ΔS_{den}, i.e. the greater the number of additional bonds formed following the introduction of a given number of residues, the higher the isokinetic temperature for the native and modified enzymes and the wider the range of experimental temperatures where $\Delta G_{den,mod} < \Delta G_{den,nat}$, i.e. the modified enzyme is more stable than the native enzyme. The activation parameters for the thermal denaturation of the enzyme vary analogously after chemical modification. If chemical modification results in an intensification of the intramolecular interactions in the enzyme globule as a result of the formation of additional bonds, then $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ for the modified enzyme are greater than for the native enzyme. "Low-temperature stabilisation" obtains in this case (Fig.7, curves *1* and *2*). With increase of inactivation temperature, the intramolecular stabilising interactions are weakened and the conformational entropy $\Delta S^{\neq}_{conf}$ increases in both the native and modified enzymes (see above). As a result of this, the difference $\Delta G^{\neq}_{den,mod} - \Delta G^{\neq}_{den,nat}$ become smaller the higher the inactivation temperature and is zero at the isokinetic temperature. Above the isokinetic temperature, the native enzyme becomes more stable than the modified enzyme.

If modification resulted in the cessation of the enzyme-stabilising interactions (in particular, on modification of groups of type III), then the structure of the enzyme becomes close to that of the denatured enzyme. $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ diminish after modification (Fig.7, curves *1* and *3*), but, by virtue of the predominance of the decrease of $\Delta H^{\neq}_{den}$ over that of $\Delta S^{\neq}_{den}$, the isokinetic temperature is in this case high and the stability of the modified enzyme is lower than that of the native enzyme virtually over the entire experimental temperature range.

Stabilisation of enzymes after immobilisation. After multipoint interaction with the carrier (covalent and non-covalent), such stabilisation is caused as a rule by the decrease of $\Delta S^{\neq}_{den}$, which predominates over the decrease of $\Delta H^{\neq}_{den}$ for thermal inactivation. This is the "high-temperature stabilisation" of enzymes[39,169–178] (Table 2). The decrease of $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ (ΔH_{den} and ΔS_{den}) after the immobilisation of

enzymes can be accounted for as follows. When the enzyme interacts with the matrix (the formation of external bonds), the bonds within its molecule are affected, which is accompanied by a decrease of ΔH_{den}. By virtue of the covalent and non-covalent fixation of the polypeptide chain at several points, this is accompanied by the simultaneous decrease of ΔS_{conf}. The greater the decrease of $\Delta S(\Delta S^{\neq})$ (the greater the number of points at which the enzyme is bound to the carrier) compared with ΔH, the lower the isokinetic temperature of the native and immobilised enzymes and the greater the temperature range in which the immobilised enzyme is more stable than the native enzyme and the greater the stabilisation effect ($\Delta G_{den,imm} - \Delta G_{den,nat}$) above the isokinetic temperature (Fig.7, curves *1* and *4*). In multipoint immobilisation the protein is probably fixed in a conformation close to that of the denatured enzyme.[168,176] This may be one of the main reasons for the low activity of enzymes after their multipoint immobilisation. In the absence of external bonds between the enzyme and the carrier (when the enzyme is incorporated in a polymer gel), the thermodynamic parameters of denaturation may not change.[174]

Enzymes functioning in membrane structures in aqueous solutions can have a conformation different from the native conformation. After a successful choice of the carrier, the structure of such protein macromolecules after immobilisation may be closer to the native structure than in solution. It is to be expected that $\Delta H^{\neq}_{den}$ and $\Delta S^{\neq}_{den}$ for such an immobilised enzyme will increase. We observed this type of experimental fact, for example, for the glow-worm luciferase immobilised on polysaccharide carriers.[175] $\Delta H^{\neq}_{den}$ was 35 kcal mol^{-1} for the enzyme in solution and 54 kcal mol^{-1} for the enzyme immobilised on Sepharose.[175] Similar effects are to be expected also for other enzymes functioning in nature in an immobilised state.

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In many cases the modification of enzymes by monofunctional agents appreciably increases their resistance to temperature, extreme pH, and organic solvents. In most cases the stabilisation effect does not exceed a factor of 10–20, but in some cases it reaches a factor of 100 and more.[108,116] In

Table 2. The changes in the thermodynamic parameters of the reversible and irreversible thermal inactivation of enzymes as a result of their modification or immobilisation.

Enzyme	$\Delta H^{\neq}$, kcal mole^{-1}	$\Delta H^{\neq}$, kcal mole^{-1}	ΔS^{0}, e.u.	$\Delta S^{\neq}$, e.u.	Stabilisation effect θ^{a}	Refs.
Peroxidase						
native	—	31	—	14	1.0(56)	[86,108]
modified by monocarboxylic acid anhydrides	—	64—87	—	110—178	32—90(56)	[86,108]
incorporated in polyacrylamide gel	—	20	—	—40	0.06(56)	[169]
α-Chymotrypsin[b]						
native	—	109	—	259	1.0	[170]
incorporated in polyacrylamide gel	—	14	—	—36	120(60)[a] T_i 48°C	[170]
incorporated in polymethacrylate gel	—	34	—	21	680(60)[a] T_i 41°C	[170]
α-Chymotrypsin native						
immobilised in soluble form on acrylic acid–maleic acid co-polymer	223	165	692	435	—	[39]
	110	38	346	44	—	[39]
immobolised on poly(maleic acid)	97	61	304	117	—	[39]
Trypsin native						
immobilised on Separon	30	67	93	142	—	[171]
with glucose	10	45	30	62	—	[171]
immobolised on cellulose	—	23	—	—6	—	[171]
β-Galactosidase						
native	—	121	—	282	1.0	[172]
immobilised on DEAE-Sephadex	—	73	—	142	0.14(60)[b] T_i=70°C	[172]
Dextran saccharase[b]						
native	—	90	—	223	1.0	[173]
innobolised on aminated glass	—	25	—	6	7.5(35) T_i=29°C	[173]
Glucoamylase[b]						
native	—	99	—	228	1.0	[174]
immobilised on sulphopropyl-Sephadex	—	64	—	126	0.12(57) T_i=70°C	[174]
Glow-worm luciferase						
immobilised on ultragel	—	35	—	40	1.0	[175]
	—	12	—	—3	0.25(25)	[175]
immobilised on BrCN-Sepharose	—	54	—	100	72(25)	[175]

[a] The temperature at which the stabilisation effect has been measured is indicated in brackets (in °C).

[b] The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as well as the stabilisation effect θ were calculated by ourselves from the temperature variations of $\lg k_{in}$ quoted in different communications.

[c] Values calculated from our own extrapolations.

[d] T_i is the isokinetic temperature.

order to attain the maximum stabilisation effect, account must be taken of those features which have been discovered by the analysis carried out in the present review. The modification of enzymes involving the introduction of carbohydrate residues, amidination, and guanidination as a rule increases the stability of enzymes (at worst it does not diminish it). The greatest influence on stability is shown by the modification involving a change in the charge of the functional groups. In addition, one must avoid the modification of internal groups (type III) of the enzyme by employing for modification the mildest possible conditions (low temperatures and minimum concentrations of organic additives), a high degree of modification, and the introduction into the enzyme of unduly bulky hydrophobic residues.

In the development of methods for stabilisation by chemical modification, it is necessary to obtain data for the thermal stability of enzymes over a wide temperature range as a function of the degree of modification and the nature of the modified groups and the modifying agent. Such analysis makes it possible to optimise not only the conditions in the preparation of the biocatalyst but also its applications. As shown above, chemically modified soluble enzymes are usually more stable at temperatures below 50–60 °C. For experiments at higher temperatures (60–70 °C), it is more desirable to employ enzymes, immobilised on polymer matrices, which are characterised by the high-temperature stabilisation, although immobilisation is frequently accompanied by a decrease of catalytic activity, in particular owing to the approach of the structure of the enzyme to that of the denatured enzyme.

The use of several additive stabilising influences, which makes it possible to achieve the greatest stabilisation effects, is extremely promising.[34]

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Faculty of Chemistry,
Moscow State University

Translated from *Uspekhi Khimii*, 53, 1891-1924 (1984) U.D.C. 543.544

Fundamentals of the Theory of Capillary Gas-Liquid-Solid Chromatography

V.G.Berezkin and P.P.Zolotarev

It is shown that the known instances of the separation of volatile compounds actually refer to gas-liquid-solid chromatography and not gas-liquid chromatography, the walls of the capillary column fulfilling the function of the solid. The theories of the retention and spreading of the chromatographic bands in elution gas-liquid-solid chromatography are examined. The results of theoretical and experimental studies indicate the need to take into account the role of adsorption in capillary gas-liquid chromatography.
The bibliography includes 140 references.

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I. INTRODUCTION

Gas–liquid chromatography is the commonest version of capillary chromatography. The retention of the chromatographed compounds in capillary gas–liquid chromatography is characterised by the same fundamental features as in gas–liquid chromatography on packed columns. It is therefore useful to examine the general theory of the retention of chromatographed compounds together with the main results of the application of this theory to capillary chromatography.

The discovery by Martin and Synge in 1941 of partition chromatography, based on the different partitions (adsorptions) of the substances to be separated between two phases, namely the mobile (gas, liquid) and stationary (liquid) phases, was an important stage in the development of chromatography.[1] In the conclusion of their communication, Martin and Synge noted that they proposed a new type of chromatography based on the partition of the solutes between two liquid phases and not on adsorption on a solid phase.[1] We may note that they also proposed[1] a new type of partition chromatography, namely gas–liquid chromatography (GLC). The first experimental study on GLC was published by James and Martin in 1952,[2] who found that the separation of the lower aliphatic acids (formic and acetic) exhibited asymmetric peaks (diffuse tails and steep fronts). This phenomenon was explained by the adsorption of the acids being separated on the surface of kieselguhr. It was shown that the adsorption can be weakened by introducing phosphoric acid into the stationary liquid phase (SLP) or by depositing it on the surface of kieselguhr (a solid carrier). Thus in the first study on GLC James and Martin should already have taken into account the phenomenon of the adsorption of the substance being separated on the solid carrier and should have taken special measures to reduce it.

Subsequently, as a result of the efforts of many investigators,[3-20] the qualitative idea concerning the role of adsorption in GLC was formulated perhaps most clearly by Dal Nogare and Juvet in a monograph.[18] In their view, adsorption on the active surface of the solid carrier is the factor responsible for the formation of tails behind the peaks. Although diatomaceous carriers are weak adsorbents compared with alumina, silica get, etc., their activity is usually sufficient for the above adsorption effect to be fully evident in the case of polar substances, for example, alcohols, water, ketones, and ethers. Adsorption on refractory brick is stronger than on celite. It is less evident in the case of non-polar substances and large relative amounts of the liquid phase and in cases where polar liquid phases, saturating the active sections of the adsorbent surface, are used.[18] An analogous view has also been expressed in the monographs of Zhukhovitskii and Turkel'taub[20] and Moshier and Sievers.[19]

We may note that capillary gas chromatography is a version of gas–liquid chromatography in which the internal walls of the capillary tube play the role of the solid carrier.

The experimental data for the adsorption of the substances separated in GLC conflicted with the view, current at the time, that GLC is a purely partition version of chromatography, and also with the theory adopted for the retention of the compounds separated in GLC, which related the retention of such compounds solely to their dissolution in the stationary liquid phase (SLP). This contradiction stimulated studies of the role of adsorption in GLC. Theoretical and experimental investigation of adsorption phenomena in GLC led to significant progress in understanding the processes occurring in chromatographic columns.

II. FUNDAMENTALS OF RETENTION THEORY

In analysing the chromatographic process in GLC, it is useful to examine primarily the model of the sorbent which can be regarded solely as an SLP. The real sorbent is a multiphase material and its simplest model is illustrated in Fig.1. The surface of the solid carrier (internal walls of the capillary column) is coated by a continuous film of the SLP of non-uniform thickness. This model of the sorbent is consistent with porometric data, mass transfer kinetic data (see, for example, Berezkin and co-workers[21,22]), data for the filling

of the pores of the solid carrier with SLP,[23] and the results of special studies based on the use of a version of the "labelled" surface method.[24] It also agrees with the results obtained in the investigation of the partition of the stationary liquid phase on the surface of the solid carrier by scanning electron microscopy.[25]

Despite its simplicity, systematic analysis of this model makes it possible to elucidate the main features of the retention of volatile compounds on a real sorbent. Indeed, it is necessary to isolate in the sorbent not one (SLP) but three phases which absorb and adsorb the substances to be separated, namely the SLP, the gas–SLP interface, and the SLP–solid carrier interface.

The equilibrium retention theory, taking into account the adsorption of the compounds to be separated, is based on a logical allowance for the contribution of the retention on individual bulk and surface phases of the real sorbent to the overall retention volume and also on the experimental test of the equations obtained (including their test by independent methods).

If the SLP layer covers fully the surface of the solid carrier, then the retention volume is determined by the equilibrium characteristics of three processes: (1) dissolution of the compound chromatographed in SLP, (2) its adsorption at the gas–SLP interface, and (3) the adsorption at the SLP–solid carrier interface. The equilibrium theory of the retention of the compounds chromatographed must take into account the contributions of all three processes indicated to the overall retention.

The need to take into account, in addition to dissolution, the adsorption of chromatographic compounds at the gas–SLP interface when an allowance is made for the contributions of these processes to retention in GLC was first pointed out by Martin,[26,27] who confirmed experimentally his postulate. An equation has been proposed[28,29] for the retention volume, which took into account both the dissolution and also the adsorption of the substance chromatographed on the surface of the solid carrier.

For the model of the sorbent with a thick SLP layer which we are considering and which usually obtains on sorbents containing more than 3% of SLP on the solid carrier, the system of equations relating to the development chromatography of one component subject to the operation of longitudinal spreading factors with allowance for absorption in the SLP and adsorption at the interfaces differs from the equation adopted previously in chromatography (see, for example, the relevant monograph[30]) by the presence of terms which take into account the adsorption at the interfaces between the SLP and the carrier gas and the solid carrier.

We shall consider the equations for the retention volume relating to the model in which the SLP covers in a continuous film the surface of the solid carrier under conditions of ideal non-linear chromatography. The system of equations for the ideal (non-equilibrium) non-linear development chromatography of one substance taking into account the adsorption of the latter on the SLP and at the interfaces can be described as follows:

$$u\frac{\partial c_g}{\partial x}+\chi_g\frac{\partial c_g}{\partial t}+\chi_{gl}\frac{\partial a_{gl}}{\partial t}+\chi_l\frac{\partial a_l}{\partial t}+\chi_{ls}\frac{\partial a_{ls}}{\partial t}=0, \quad (1)$$

$$a_{gl}=f_{gl}(c_g), \quad (2)$$

$$a_l=f_l(c_g), \quad (3)$$

$$a_{ls}=f_{ls}(a), \quad (4)$$

where u is the linear flow rate of the carrier gas, x the coordinate, t the time, c_g the volume concentration of the chromatographed substance in the gas phase, a_l the volume concentration of the substance in the SLP, a_{ls} the surface concentration of the substance at the SLP–solid carrier interface, χ_g the fraction of the gas phase along the column cross-section, χ_l the fraction of the liquid phase along the column cross-section, χ_{gl} the ratio of the area of the SLP–solid carrier interface to the volume of the sorbent, and a_{gl} the surface concentration of the test substance at the gas–SLP interface.

Eqns.(2) and (4) are the equations of the adsorption isotherms of the chromatographed compound at the SLP–solid carrier and gas–SLP interfaces and Eqn.(3) is that of the isotherm of absorption (dissolution) in the SLP. Eqn.(1) differs from that usually considered (see, for example, Rachinskii[30]) by the presence of two additional terms – the third and the fifth. The introduction of these terms made it possible to take into account the adsorption at the interface between the SLP and the carrier gas and the solid carrier.

The solution of the above system of equations on the assumption of the carrier gas pressure drop along the length of the chromatographic column is small so that the correction for the compressibility of the carrier gas can be disregarded, yields the following equation for the pure retention volume:

$$V_N=V_R^0-V_M=f'_{gl}S_l+f'_lH_l+f'_lf'_{ls}S_s, \quad (5)$$

where $f'_{gl}=da_{gl}/dc_g$, $f'_l=da_l/dc_g$, $f'_{ls}=da_{ls}/da_l$, S_l is the area of the gas–SLP interface for the sorbent in the column, H_l the volume of the SLP in the column, S_{ls} the area of the SLP–solid carrier interface, V_N the pure retention volume,

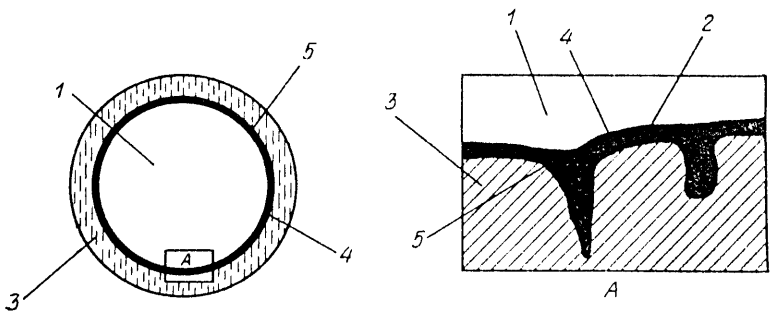


Figure 1. A simplified model of the real sorbent in capillary GLC: 1) gas phase; 2) SLP; 3) solid carrier (wall of capillary column); 4) gas–SLP interface; 5) SLP–solid carrier interface.

V_R the retention volume, and V_M the dead volume of the column. If the adsorption and absorption isotherms are linear, the derivatives f'_{gl}, f'_l, and f'_{ls} are constant.

Eqn.(5) establishes the relation between the retention volume and the characteristics of the sorbent employed taking into account the dissolution in the SLP and the adsorption at its interfaces. It follows from this equation that the retention volume in equilibrium chromatography is an additive function of the retention volumes in the separate phases of the real sorbent. We may note that previously Giddings[31] proposed an additive equation for the second quantity (the lag factor) characterising the relative retention (R_f), which is used widely in thin-layer chromatography.

There is also a possibility of another derivation of the additivity equation for the ideal non-linear chromatography based on Wicke's Law using the adsorption isotherms for a real complex sorbent in its equation. In this case the sorption also consists of the adsorption at the SLP interfaces and the dissolution in the SLP film.

Since in the general case the real sorbent may contain not three but a significantly greater number of phases, each of which is capable of retaining the chromatographed compounds, the relations obtained above can be usefully extended to the case of a large number of phases. Within the framework of ideal non-linear chromatography (i.e. on the assumption of the instantaneous establishment of equilibrium and of the absence of diffusional spreading effects), it has been shown[32,33] that the pure retention volume V_N in a real multiphase sorbent consists of the sum of the partial retention volumes V_{li} and V_{sj} due respectively to the adsorption and absorption of the chromatographed substance on the individual phases of the sorbent:

$$V_N = \sum_{i=1}^{m} V_{li} + \sum_{j=1}^{n} V_{sj} \qquad (6)$$

or

$$V_N = \sum_{i=1}^{m} K_{li} H_{li} + \sum_{j=1}^{n} K_{sj} S_{sj}, \qquad (7)$$

where K_{li} is the constant for equilibrium of the test substance between the mobile phase and the SLP of the ith type, H_{li} the volume of the SLP of the ith type in the chromatographic column (for example, the volume of the macrolayer or microlayer in the liquid phase on the surface of the solid carrier, the volume of the liquid phase in the micropores, etc), K_{sj} the constant for equilibrium of the test substance between the stationary phase and the jth type interface, and S_{sj} the area of the jth type interface in the column (for example, the gas–solid carrier, SLP–solid carrier, gas–SLP, etc. interfaces).

Eqns.(6) and (7) are fairly general. It can be shown that the known equations for the retention volume are special cases of these equations. For specific values of the parameters i and j, it is possible to obtain directly from Eqn.(7) the familiar equations for the retention volume: the equation of the traditional GLC (see, for example Dal Nogare and Juvet[18]); the equation taking into account the dissolution and the adsorption at the gas–SLP interface,[26] the equation taking into account the dissolution and adsorption at the SLP–solid carrier interface;[28] the equation taking into account the dissolution and adsorption of the sorbate on the SLP–solid carrier and SLP–carrier gas interfaces;[32] the equation reflecting the interaction between the sorbate and the solid alone;[34] the equation taking into account only the adsorption at the gas–SLP interface;[35] the equation for the retention volume on complex sorbents (for example, a solid carrier combined with an adsorbent modified by the SLP).[36]

If the adsorption isotherm is described by a non-linear equation, then in this case Eqns. (6) and (7) are valid only within the framework of ideal non-linear chromatography, which naturally limits their applicability. However, one should note that development gas-chromatographic methods for the determination of non-linear adsorption isotherms, developed on the basis of ideal non-linear chromatography, have been used successfully in chromatographic practice and the results obtained are independent of the carrier gas flow rate, the sample size, etc. In gas–solid chromatography the adsorption isotherms measured by the gas-chromatographic and static methods mentioned above are in good agreement with one another (see, for example, Kiselev and Yashin[34] and Roginskii et al.[37]). The region of the applicability of Eqns. (6) and (7) is therefore fairly broad also for non-linear isotherms.

When the general Eqns.(6) and (7) are used, it is necessary in the general case to resort to data for the phase characteristics of the sorbent employed and for the distribution of the SLP on the surface of the solid carrier. In the case occurring commonly in chromatographic practice, where the surface of the solid carrier is fully coated by a macrofilm of the liquid, Eqn.(8), which is a corollary of Eqn.(5), is therefore used most frequently:

$$V_{Ns} = K_l H_{ls} + K_{gl} S_{ls} + K_{ls} S_{ss}, \qquad (8)$$

where V_{Ns} is the retention volume referred to 1 g of the solid carrier, K_l, K_{gl}, and K_{ls} are the constants for equilibrium of the chromatographed substance between the SLP and the gas phase, between the SLP–gas interfacial phase and the gas phase, and between the SLP–solid carrier interfacial phase and the SLP respectively, H_{ls} is the volume of the SLP in the column referred to 1 g of the solid carrier, S_{ls} and S_{ss} are the areas of the SLP–gas and solid carrier SLP interfaces referred to 1 g of the solid carrier respectively, $K_l = a_l/c_g$, $K_{gl} = a_{gl}/c_g$, and $K_{ls} = a_{ls}/a_l$.

Eqn.(8) establishes the relation between the retention volume and the characteristics of the sorbent used. The retention volume in equilibrium linear chromatography with operation of longitudinal spreading factors is an additive function of the retention in the individual phases of the real sorbent. The first term of this equation reflects the contribution of the adsorption of the chromatographed substance on the SLP, the second term the contribution of the adsorption on the gas–SLP interface, and the third term the contribution of the absorption of the SLP–solid carrier interface.

Table 1 presents the main stages in the development of ideas about adsorption in GLC along three main pathways: theory, chromatographic experiment undertaken to test the theory, and independent experimental tests of the theory by non-chromatographic methods. Naturally, the isolation of specific stages in the development of ideas about the role of adsorption in GLC is fairly subjective. Like any important trend in science, it arose and developed by virtue of the investigations of many workers from different countries. The work of Nikolov,[52,53] Suprinowicz, Waksmundski, Rudzinski, and co-workers,[54–56] Hüber and Gerritse,[57] Eon and Guiochon, [58,59] Kovats and co-workers,[60] and many other investigators[61–86] has also made an important contribution to the study of the role of adsorption in GLC. Thus, revolutionary changes involving the study of adsorption phenomena have occurred in the last two decades in the ideas concerning the mechanism of the retention of chromatographed compounds in GLC as a result of the work of many investigators from different countries.

The view that adsorption on the surface of the solid carrier (walls) in capillary chromatography is negligible and can be neglected has been expressed fairly frequently. Investigators sharing this view usually adduce the following arguments in its defence. Firstly, the surface of the capillary column (glass, quartz, stainless steel) is more inert than the surfaces of solid carriers used in packed columns and the chromatographic bands in capillary chromatography are as a consequence usually more symmetrical than in packed columns.

Table 1. The principal stages in the development of ideas concerning the role of adsorption in GLC.

Stage	Characteristic	Refs.
Adsorption at gas–SLP interface	Theory	[26]
	Experiment	[26]
	Independent test	[27]
Adsorption at SLP–solid carrier interface	Theory: linear isotherm	[28, 31]
	Theory: non-linear isotherm	[32, 39]
	Experiment: determination of isotherm	[40, 41]
	Experiment: determination of heat of adsorption	[42]
	Independent test	[43, 45]
Joint determination of the contribution of adsorption at gas–SLP and SLP–solid carrier interfaces	Theory and experiment	[32]
The influence of adsorption on the relative retention parameters (relative retention time and Kovats retention index)	Theory and experiment	[33, 46]
Retention on sorbents with thin SLP films (less than 3% on solid carrier)	Theory and experiment	[47, 48]
Adsorption in open capillary columns	Theory and experiment	[49, 51]

Secondly, the ratio of the volume of the SLP to the surface area of the solid carrier is usually greater in capillary chromatography than in packed columns, which should decrease the contribution of adsorption to the overall retention volume. As regards the first argument, glass and quartz surfaces cannot be regarded as inert with respect to adsorption. Experimental data have shown that even the most inert quartz columns exhibit distinct adsorption properties in relation to polar compounds (see, for example, Jennings[87]). One should also note that the symmetry of the chromatographic band is only a necessary but not a sufficient condition for the adsorption inertness of the given surface in relation to a given compound under the given conditions. Furthermore, glass (and other) surfaces are frequently subjected to a preliminary treatment whose purpose is to roughen the surface, which increases its adsorption capacity. The second argument does not appear to be convincing for the following reason. On average, the separation temperature in capillary chromatography is lower by ~50–100 °C than the separation temperature in packed columns. Since the heat of adsorption of polar chromatographed compounds when non-polar SLP are used is several times higher than the heat of solution, a significant decrease of the separation temperature causes a relative increase of the contribution of adsorption to the retention compensating at least partially the increase of the thickness of the SLP layer. We may note that the retention volume varies exponentially with the heat of the decisive chromatographic processes and linearly with the thickness of the SLP film, i.e. the heat of the process has a more significant influence on the retention.

Yet another factor enhancing the degree of adsorption in capillary chromatography is noteworthy: the resolving capacity of the capillary column is ~5–10 times higher than that of a packed column. Indeed it is known (seen, for example, Dal Nogare and Juvet[18]) that the separation factor for two compounds R is a function of the following characteristics of the chromatographic column employed:

$$R = \frac{N^{1/2}}{4}\left(\frac{\alpha-1}{\alpha}\right)\frac{k}{k+1}\ , \qquad (9)$$

where N is the number of theoretical plates of the column, α the column selectivity (the relative retention of the compounds separated), and k the capacity coefficient. The ratio of the separation factors in capillary (R_{cc}) and packed (R_{pc}) columns can be represented by the following relation:

$$\frac{R_{cc}}{R_{pc}} = \frac{(\alpha_{cc}-1)}{(\alpha_{pc}-1)}\cdot\frac{\alpha_{cc}}{\alpha_{pc}}\cdot\frac{k_{cc}}{k_{pc}}\cdot\frac{k_{pc}+1}{k_{cc}+1}\cdot\left(\frac{N_{cc}}{N_{pc}}\right)^{1/2}\ , \qquad (10)$$

where the subscripts cc and pc refer respectively to quantities characterising the capillary and packed columns.

Since the first terms of Eqn.(10) are close to unity and $N_{cc} \cong 60 \times 10^3$ and $N_{pc} \cong 10^3$, we obtain in accordance with Eqn.(10).

$$\frac{R_{cc}}{R_{pc}} \simeq \left(\frac{60\cdot 10^3}{10^3}\right)^{1/2} \simeq 8\ . \qquad (11)$$

Thus, under the conditions examined above, the width of the chromatographic band in a capillary column is 10 times smaller than in a packed column. This means that the real accuracy of the measurements of the retention using capillary columns is 10 times greater than for packed columns; even small contributions of adsorption to the retention have a greater importance in capillary chromatography owing to the greater resolving capacity of the latter.

We shall consider certain most important consequences arising from allowance for adsorption phenomena in GLC.

III. THE INTERACTION OF THE SOLUTE WITH THE STATIONARY LIQUID PHASE UNDER THE CONDITIONS OF THE ADSORPTION OF THE CHROMATOGRAPHED SUBSTANCES AT THE STATIONARY LIQUID PHASE INTERFACES

In his Nobel Lecture in 1952 Martin noted that the application of the chromatographic method and apparatus makes it possible to measure fairly simply the free energies of solution of volatile compounds in the SLP and thus to investigate successfully the molecular forces in solutions.[88] The development of GLC fully confirmed the validity of this prediction, but the correct employment of the methods for the investigation of the interaction of the solute and the involatile SLP, which have been thoroughly developed in gas chromatography is possible only when the contribution determined solely by the dissolution of the chromatographed substance in the SLP is isolated from the overall retention volume. For example, in order to determine V_{gtl}, which is the initial quantity needed to determine the specific retention volume due solely to the dissolution of the test substance in the SLP, it is useful to employ Eqn.(12):

$$V_{gt} = \frac{V_N}{W_l}\ , \qquad (12a)$$

$$V_{gt} = \frac{V_{NL}}{W_l} + \frac{1}{W_l}\sum_{i=2}^{n} V_{Ni}\ , \qquad (12b)$$

$$V_{gtl} = \frac{V_{Nl}}{W_l}\ , \qquad (12c)$$

where $V_{gtl} = V_{gl}\ (273/T)$, V_{gl} is the specific retention volume due solely to the dissolution of the volatile substance in the SLP, V_{Nl} the part of the pure retention volume due solely to the dissolution of the chromatographed substance in the SLP macrolayer, W_l the mass of the SLP in the column, and V_{Ni} the part of the pure retention volume due to the retention of the volatile substance by the ith phase of the sorbent (with exclusion of the SLP macrolayer).

Fig. 2 presents the ratios $\psi = V_g$ (refractory brick)$/V_{gt}$ (Chromosorb W) and $\psi_l = V_{gil}$ (refractory brick)$/V_{gt}$ (Chromosorb W) which we calculated[21] from the experimental data of Pecsok et al.;[14] the type of the solid carrier used to prepare the sorbent is indicated in brackets. The calculation was performed by Eqn. (12c) and also by the traditional method, i.e. by Eqn. (12a). The data presented in Fig. 2 were obtained for sorbents containing ~8.8% of the SLP.

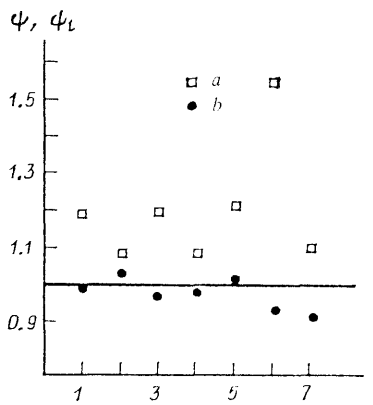


Figure 2. Dependence of ψ (points *a*) and ψ_l (points *b*) on the nature of the chromatographed compounds; the numerals along the abscissa axis denote the chromatographed compounds: 1) propionaldehyde; 2) benzene; 3) ethyl acetate; 4) acetone; 5) ethyl methyl ketone; 6) hex-1-ene; 7) cyclohexene. The $\psi_l = 1.0$ straight line, corresponding to the complete compensation of adsorption and other effects, is shown.

It follows from the results presented that the extrapolation method, taking into account adsorption, yields stable constant values of ψ_l, which are independent of the type of solid carrier, while the values of ψ obtained by the traditional method do depend on the type of solid carrier and higher values for the sorbent are obtained using refractory brick, which has a higher adsorption activity, as the solid carrier.

We may note that the contribution of adsorption to the overall retention volume is appreciable for the series of systems (solid carrier–SLP–sorbate) usually employed in GLC (Table 2).[21,22,24,36] Thus, in a quantitative study of the interaction of the solute with the SLP, it is essential either to take into account adsorption or to show that it can be neglected compared with dissolution.

We shall consider the main results obtained using the additive theory of retention in capillary chromatography. In the first quantitative study[49] of the contribution of adsorption to retention in capillary chromatography, the experimental data of Brunner and Cartoni[79] were used to test the applicability of the theory.[32] It was shown that the retention theory developed previously can be applied successfully also to capillary chromatography. Fig. 3 illustrates the dependence of V_N^0/W_l on $1/W_l$, which is described satisfactorily by the equation:

$$\frac{V_N^0}{W_l} = V_g + A\frac{1}{W_l}, \qquad (13)$$

where A is a coefficient characterising the contribution of adsorption to retention and V_N^0 the pure retention volume adjusted to 0 °C and a pressure of 1 atm. Eqn. (13) is a corollary of the general Eqn. (8) when the contribution of adsorption can be regarded as constant. Eqn. (13) can be usefully employed to determine the specific retention volume V_g, which is normally used in various physicochemical calculations (see, for example, Dal Nogare and Juvet[18] and Conder and Young[89]).

Table 2. Estimation of various contributions to the overall retention volume.

Chromatographic system	*a*	*b*	*c*	*d*	*e*
Refractory brick (INZ-600)–Apiezon K–benzene	60	150	57	—	43
Chromosorb P–stearic acid–n-hexane	72	63	75	5.0	20
Chromosorb W–stearic acid–n-hexane	72	65	81	—	19
Polychrom-1–diethylene glycol succinate–diethylene glycol	138	3509	80	20	—
Graphitised black–squalane–cyclohexa-1,4-diene	28	980	72	—	28
Bentone-245–di-iso-octyl sebacate–benzene	50	380	15	—	85
Refractory brick–ββ-thiodipropionitrile–heptane	25	18	25	67	8.0
Chromosorb W–ββ-thiodipropionitrile–heptane	25	19.9	54	42	4

Notation: *a*) temperature (degrees C); *b*) distribution constant of the sorbate in the gas–SLP system; *c*) contribution of dissolution to the retention volume (%); *d*) contribution of adsorption at the gas–SLP interface (%); *e*) contribution of adsorption at the SLP–solid carrier interface.

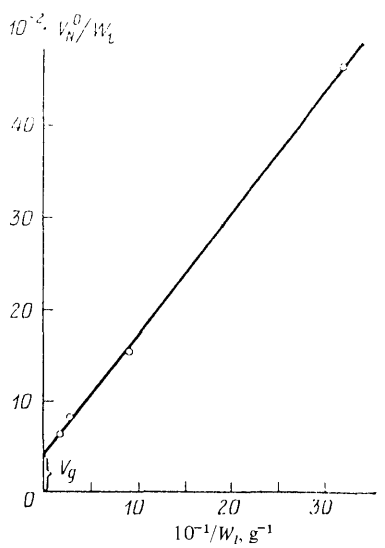


Figure 3. Dependence of V_N^0/W_l on $1/W_l$ (according to the experimental data of Brunner and Cartoni[79]).

It is noteworthy that the glass capillary columns used by Berezkin et al.[49] had a high internal surface area; the pure retention volume of heptane at 40 °C on a 38 m column (0.22 mm in diameter) was 14.7 ml. Furthermore, the absolute retention volumes are quoted by Brunner and Cartoni[79] only for one hydrocarbon (n-heptane). It therefore appeared essential, firstly, to investigate the role of adsorption in capillary columns which do not exhibit such a high adsorption activity and, secondly, it was necessary to develop rational forms of the equations of the additive theory to calculate retentions specifically in capillary chromatography. The latter task was undertaken because the use of the absolute mass or volume of the SLP in capillary chromatography presents certain difficulties.

The following study of the role of adsorption in capillary columns was therefore carried out for aromatic hydrocarbons and paraffins in the perdeuteriosqualane–stainless steel system.[50]

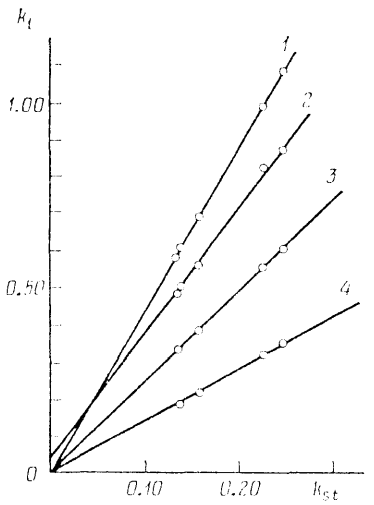


Figure 4. Dependence of k_i on k_{st} for hydrocarbons on a stainless steel column (standard–n-heptane): chromatographed substance: 1) cyclohexane; 2) benzene; 3) n-hexane; 4) 2,2-dimethylbutane.

Using the general Eqn.(8) obtained previously and assuming that the retention volume is independent of the sample size, that the properties of the thick SLP layer do not differ from those of the corresponding bulk phase, that the area of the gas–SLP interface hardly changes with increase of the thickness of the SLP film on the inner wall of the column, and that the SLP film covers the entire internal surface of the column, it is possible to obtain by means of simple transformations, the following equations, which can be usefully employed for the quantitative estimation of the role of adsorption in capillary chromatography:

$$V_{ri} = \frac{V_{Ni}}{V_{N,st}} = \frac{K_{li}}{K_{l,st}} + \frac{A_i}{V_M} \cdot \frac{1}{K_{st}} , \qquad (14)$$

where V_{ri} is the relative retention volume of the ith substance, A_i a coefficient reflecting the contribution of adsorption to the relative retention volume, and k_{st} the extraction coefficient or the capacity coefficient of the compound adopted as the standard. The standard compound is chosen in such a way that its retention is determined virtually only by the dissolution in the SLP and adsorption can be neglected, i.e. so that the relation $V_{N,st} = K_{l,st}\ H_l$ (H_l is the volume of the SLP in the column) holds. The capacity coefficient and not the relative retention volume can be usefully employed in many instances as the determining quantity. Eqn.(14) can then be expressed in the following form:

$$k_i = \frac{A_i}{V_M} + \frac{K_{li}}{K_{l,st}} \cdot k_{st} . \qquad (15)$$

The parameters of Eqns.(14) and (15) can be determined graphically, for example. The limiting retention is then of greatest interest:

$$V_{rli} = \frac{K_{li}}{K_{l,st}} . \qquad (16)$$

The limiting retention V_{rli} can be used as the initial retention for various calculations characterising the sorbate–SLP interaction and, by resorting to the absolute thermodynamic parameters for one compound (the standard), it is possible to obtain the absolute values of the physicochemical characteristics of all the compounds used in the chromatographic experiment.

Eqns.(14)–(16) have been used to interpret experimental data obtained in Keulemans' laboratory.[50] A stainless steel capillary column 100 mm long and with an internal diameter of 0.25 mm was used; the SLP was perdeuteriosqualane; the column temperature was 70 °C. Fig.4[50] presents the experimental results obtained on this column; it is seen that Eqn.(15) describes the experimental data satisfactorily. Calculation by Eqn.(15) makes it possible to determine the limiting relative retention V_{rli} and to estimate the contribution of adsorption to the retention.

Table 3[50] presents the parameters of Eqn.(15) evaluated by the method of least squares (on a computer). For the saturated hydrocarbons investigated, including cyclic hydrocarbons, adsorption can be neglected. However, adsorption exerts a significant influence on the retention of aromatic compounds, for example, benzene. For example, $V_{rli} = 3.42$ for benzene, while the limiting retention index is 636.0; the experimental retention indices of benzene determined on this column amounted to 639.8–643.8.[50]

Table 3. The ratio of the distribution constants and the adsorption characteristic of the sorbate for a stainless steel capillary column [parameters of Eqn.(15)].[50]

Compound	$K_{li}/K_{l,st}$	A_i/V_M
n-Pentane	1.000	0.000
2,2-Dimethylbutane	1.438	−0.004
2,3-Dimethylbutane	1.888	−0.004
3-Methylbutane	2.184	−0.004
n-Hexane	2.469	+0.002
Methylcyclopentane	3.250	−0.003
Benzene	3.418	−0.033
Cyclohexane	4.480	−0.008
3-Methylhexane	4.939	−0.008
n-Heptane	5.968	+0.010

Thus the additive theory of retention is fully applicable also in capillary chromatography. Exact measurements of the ratio of the partition constants of the chromatographed compounds in gas–liquid capillary chromatography are possible only when account is taken of the contribution of adsorption.

IV. THE ADSORPTION OF VOLATILE COMPOUNDS

Gas chromatography has been used traditionally as a physicochemical method for the investigation of adsorption on solid adsorbents from the gas phase.[34] Since the adsorption of chromatographed compounds at the interfaces between the SLP and the carrier gas and the solid carrier influences their retention volumes [see Eqns.(7) and (8)], the above relations can be used for the quantitative study of the adsorption of volatile compounds at the gas–SLP and SLP–solid carrier interfaces.

Many investigators have studied the influence of adsorption on the retention indices. As an example, Table 4 presents data for the relative retention of methyl oleate, methyl linoleate, and methyl linolenate on Rheoplex 400 using different solid carriers, including a stainless steel capillary column.[70] It follows from the data presented in Table 4 that the solid carrier (in the first place the area and type of its surface) exerts a significant influence on retention.

Table 4. The influence of the solid carrier (SLP–Rheoplex 400) on the retention of the methyl esters of unsaturated C_{18} acids (standard–methyl stearate).[70]

Solid carrier	Relative retention time		
	methyl oleate	methyl linoleate	methyl linolenate
Gas-chrom P, silanised	1.10	1.33	1.71
Chromaton N AW HMDS	1.10	1.32	1.70
Gas-chrom Q	1.09	1.31	1.70
Chromosorb W, silanised	1.09	1.32	1.69
Chromosorb P, silanised	1.10	1.32	1.70
Chezasorb AW HMDS	1.09	1.31	1.68
Chromosorb G AW	1.09	1.31	1.64
Celite 545	1.08	1.29	1.60
Chromosorb W	1.06	1.28	1.62
Chromosorb P	1.05	1.23	1.54
Kieselguhr	1.07	1.27	1.62
Capillary column*	1.10	1.32	1.69

*Stainless steel.

The development of methods for the quantitative assessment of adsorption phenomena in GLC has led to fundamental new possibilities in the investigation and quantitative measurement of the degrees of adsorption of volatile substances, in the first place at the gas–liquid interface and in the second place at the SLP–solid carrier (solid) interface.

After the determination of the dependence of the partial retention volumes on concentration, which is in its turn determined by the adsorption at the interfaces between the SLP and the gas and the solid, it is possible to calculate the adsorption isotherms at the gas–SLP and the SLP–solid interfaces using the following equation:[90]

$$a_{sj} = \frac{1}{S_{sj}} \int_0^c V_{sj}(c)\,\mathrm{d}c \ , \qquad (17)$$

where a_{sj} is the concentration of the test substance in the stationary surface phase of the jth type, S_{sj} the surface area of the surface phase of the jth type, and $V_{sj}(c)$ the partial retention volume of the test substance when its concentration in the mobile phase is c.

The methods for the "isolation" of the pure partial retention volumes from the overall retention volume and the methods for the determination of the isotherms have been described in detail.[24,36,43,90–92] As an example, Fig.5[43] presents the isotherm for the adsorption of *p*-xylene on the dimethyldioctadecylammonium derivative of vermiculite impregnated with di-iso-octyl sebacate, which has been obtained gas-chromatographically at 65 °C, as well as the experimental points for the same system obtained from static experiments. The results of the gas-chromatographic and static experiments agree satisfactorily. Other examples of analogous experiments for solid carriers have been published elsewhere.[44,45]

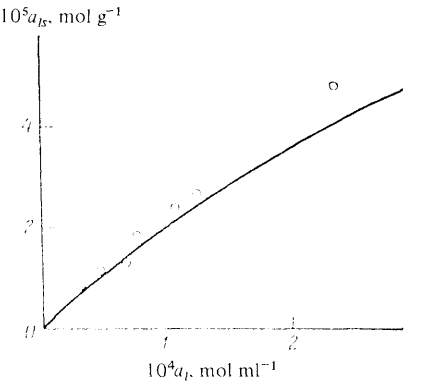


Figure 5. Isotherm for the adsorption of *p*-xylene on methyldioctadecylammonium vermiculite from solutions in di-iso-octyl sebacate; continuous line–adsorption isotherm according to gas-chromatographic data; circles–data obtained by a static method.

For linear dissolution and adsorption isotherms, the retention volume depends on the characteristics of the adsorption in accordance with Eqn.(8). Having determined experimentally the dependence of the retention volume on the content of the SLP on the solid carrier V_{Ns} on H_{ls} and the dependence of the area of the gas–SLP interface S_{ls} on H_{sl} as well as the surface area of the solid carrier S_s, it is possible to determine the adsorption coefficients K_{gl} and K_{ls}; the methods of calculation have been described.[24,32,91]

Table 5. Heats of solution (ΔH_s) in Apiezon K and adsorption (ΔH_a) at the Apiezon K–INZ-600 (solid carrier) interface measured by the gas-chromatographic method.[42]

Compound	ΔH_s, kcal mol^{-1}	ΔH_a, kcal mol^{-1}
n-Hexane	5.8	4.6
Hex-1-yne	5.2	10.9
n-Heptane	6.6	7.6
Hept-1-yne	8.6	17.8

The procedures proposed[42] for the measurement of the dissolution coefficients of volatile compounds in the SLP and of the adsorption coefficients on the SLP–solid carrier interface made it possible to determine the heats of solution and adsorption from the temperature variation of these coefficients. Table 5[42] presents the results of the determination of the

heats of solution and adsorption for a sorbate–refractory brick (INZ-600)–Apiezon K system. It follows from the results that the heats of adsorption of alkynes are much higher than the heats of solution, which can be accounted for by their specific interactions with the silanol surface groups.

In order to test the ideas developed, measurements have been made[32] by gas–liquid and liquid chromatography of the adsorption coefficients K_S at the SLP–solid interface for the hexadecane–Chromosorb P and hexadecane–Chromosorb W systems at 26 °C. The adsorption coefficients measured by these two independent methods are close to one another. For example, the K_S obtained by the GLC and liquid chromatographic methods for benzaldehyde in the hexadecane–Chromosorb P system are 0.091 and 0.090 $cm^3\ g^{-1}$; the values for ethyl methyl ketone in the hexadecane–Chromosorb W system are respectively 0.109 and 0.09 $cm^3\ g^{-1}$, and those for pyridine in the hexadecane–Chromosorb W system are respectively 0.165 and 0.164 $cm^3\ g^{-1}$. Hence an independent test of the proposed methods confirmed their validity.[45] Thus, using the methods developed, it is possible to calculate not only the partition (absorption) isotherms but also the (adsorption) isotherms at the SLP isotherms. which is a fundamentally new physicochemical application of chromatography.

It has been found that the influence of adsorption on the separation has not only a physicochemical but also an analytical application. The influence of adsorption on the separation in capillary gas–liquid chromatography has been investigated by Sojak and Berezkin.[93] Since the resolution in capillary columns is greater than in packed columns by a factor of 5–10, even relatively small changes in the contribution of adsorption can induce an appreciable change in the separation up to an alteration of the order in which the components emerge. Therefore allowance for and employment of the adsorption factor is particularly justified, in our view, for the improvement of the separation in gas–liquid capillary chromatography. The sorbate-adsorbent adsorption interactions are of a type fundamentally different from that of the sorbate–SLP interaction and are particularly sensitive to the structure of the compounds separated (see, for example, Kiselev and Yashin[34]). The change in the separation can be a result of the ageing of the columns, a change in the content of the SLP in the capillary column, an increase in the adsorption activity of the internal surface of the column, or a change in the adsorbent present in the SLP layer.

Since the separation depends significantly on the selectivity of the sorbent employed, whose measure is the relative retention, it is useful to examine the dependence of the selectivity α on the degree of adsorption in the capillary column:

$$\alpha = \frac{V_{N1}}{V_{N2}} = \frac{K_{l1}}{K_{l2}} \cdot \frac{1 + a_1/H_l}{1 + a_2/H_l}\ , \qquad (18)$$

where

$$a_1 = \frac{K_{gl1}S_l + K_{l1}K_{ls1}S_s}{K_{l1}}\ ;$$

$$a_2 = \frac{K_{gl2}S_l + K_{l2}K_{ls2}S_s}{K_{l2}}\ .$$

The subscripts 1 and 2 in Eqn.(18) refer to the compounds separated (the first and second respectively). Having expanded this expression in a Maclaurin's series in terms of the variable $1/H_l$, we obtain

$$\alpha = \frac{K_{l1}}{K_{l2}} + \frac{K_{l1}}{K_{l2}}(a_1 - a_2) \cdot \frac{1}{H_l}\ . \qquad (19)$$

Depending on the relative values of the degrees of adsorption ($a_1 > a_2$ or $a_1 < a_2$), the quantity α can increase or decrease with increase of H_l. For components with similar properties, whose separation is of interest, one can assume that $K_{l1}/K_{l2} \cong 1$; we then obtain

$$\alpha - 1 \simeq \frac{K_{l1}}{K_{l2}}(a_1 - a_2) \cdot \frac{1}{H_l} \simeq (a_1 - a_2) \cdot \frac{1}{H_l}\ . \qquad (20)$$

On substituting this expression in Eqn.(9), we obtain

$$R \simeq \frac{1}{4} N^{1/2} \cdot \frac{k}{1+k} \cdot \frac{a_1 - a_2}{H_l}\ . \qquad (21)$$

Thus in the case which we have considered the separation factor depends significantly on the ratio of the difference between the adsorption terms of the retention to the amount of SLP in the capillary column.

Fig. 6[93] presents chromatograms illustrating the influence of the adsorption factor on the separation. A change in the thickness of the SLP layer alters the ratio of the adsorption and absorption factors, which alters the separation. A mixture of pentadecene isomers has been separated on two glass columns *A* and *B*. Comparison of the chromatograms shows that the order of the emergence of *trans*-pentadec-6-ene and *cis*-pentadec-5-ene separated in the two columns is different.[93] The capacity coefficient, which reflects the thickness of the SLP film is 2.1 in column *A* and 1.3 in column *B* for *cis*-pentadec-5-ene, i.e. the difference is not very great. The difference between the retention indices for these isomers is 1.2 in column *A* and 0.9 in column *B*.

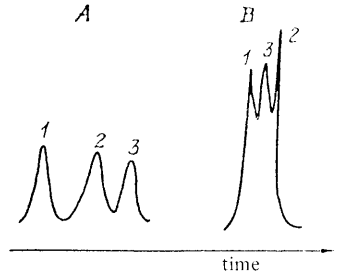


Figure 6. The influence of the thickness of the SLP layer on separation in capillary gas–liquid chromatography.[93] Separation conditions: 300 m × 0.25 mm glass columns *A* and *B*; SLP–Carbowax 20M; temperature 95 °C; the thickness of the SLP layer is greater in column *A*; compounds: 1) *trans*-pentadec-7-ene; 2) *trans*-pentadec-6-ene; 3) *cis*-pentadec-5-ene.

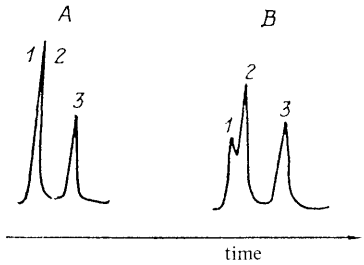


Figure 7. The influence of the adsorption activity of the column on separation.[93] Separation conditions: 100 m × 0.2 mm glass capillary columns; SLP–Apiezon L; temperature 164 °C; compounds: 1) n-heptadecane; 2) *trans*-heptadec-2-ene; 3) *cis*-heptadec-2-ene.

Fig. 7 illustrates the separation of *cis*-heptadec-2-ene and *trans*-heptadec-2-ene and n-heptadecane on two glass capillary columns *A* and *B*.[93] The adsorption activity of the internal surface of column *B* is appreciably higher than that

of column *A*, which accounts for the successful separation of *trans*-heptadec-2-ene and n-heptadecane on column *B*.

The examples presented show that adsorption can exert a significant influence (both positive and negative) on the separation of the compounds analysed, including compounds with similar properties, for example, isomers, in capillary chromatography.

V. METHODS FOR THE IDENTIFICATION OF CHROMATOGRAPHIC BANDS TAKING INTO ACCOUNT THE ADSORPTION PHENOMENA IN GAS–LIQUID–SOLID CHROMATOGRAPHY

The qualitative interpretation of the chromatograms of complex organic mixtures is an important stage in gas-chromatographic analysis. The identification methods, based on a comparison of the experimental retentions of the unknown compounds chromatographed with the available literature data, are widely used in gas-chromatographic analytical practice. However, the application of this simple and effective method is restricted owing to the inadequate reproducibility of the retention parameters in different laboratories.

The retention theory developed above makes it possible to explain a number of causes of the non-reproducibility of the retentions and suggests new effective chromatographic methods for the identification of compounds.

In the general case the relative retention can be expressed by the equation

$$\frac{V_N}{V_{N,st}} = \frac{K_l}{K_{l,st}} \cdot \frac{1 + \left(\sum_{i=2}^{m} K_{li} H_{li} + \sum_{j=1}^{n} K_{sj} S_{sj} \right) (1/K_l H_l)}{1 + \left(\sum_{i=2}^{m} K_{li,st} H_{li} + \sum_{j=1}^{n} K_{sj,st} S_{sj} \right) (1/K_{l,st} H_l)} , \qquad (22)$$

where $V_{N,st}$ is the true retention volume of the substance adopted as the standard $K_{l,st}$ the constant of the equilibrium involving the standard substance between the SLP and the gas phase, $K_{sj,st}$ the constant for the equilibrium involving the standard substance between the SLP and the *j*th type interface, and $K_{li,st}$ the constant of the equilibrium involving the standard substance between the *i*th type SLP and the mobile phase.

Apart from dissolution processes, Eqn.(22) takes into account the adsorption interactions associated with the properties of the solid carrier and the phase characteristics of the sorbent. It follows from Eqn.(22) that the relative retention is not a constant for a given chromatographed compound and cannot be used for qualitative analysis on the basis of literature data. The modification of solid diatomaceous carriers or the employment of polymeric solid carriers lead in many instances solely to a decrease of the role of adsorption phenomena, but the contribution of adsorption to the retention frequently remains appreciable.

If the retention volume is determined solely by the dissolution of the chromatographed substance in the SLP and by the adsorption at the interfaces between the SLP and the mobile phase in the solid carrier [see Eqn.(8)], then the relative retention volume can be expressed by the equation

$$\frac{V_N}{V_{N,st}} = \frac{K_l}{K_{l,st}} + \lambda_1 \frac{1}{H_l} , \qquad (23)$$

where

$$\lambda_1 = \frac{(K_{gl} K_{l,st} - K_{gl,st} K_l) S_{ls} + (K_s - K_{s,st}) K_l K_{l,st} S_s}{K_{l,st}^2} . \qquad (24)$$

It is desirable to select as the standard a substance for which the retention is determined solely by dissolution, i.e. $V_{N,st} = K_{l,st} V_l$; in this case we obtain

$$\lambda_{10} = \frac{K_{gl} S_{ls} + K_l K_s S_s}{K_{l,st}} . \qquad (25)$$

Eqn.(23) is linear in $1/H_l$ and makes it possible to determine the relative distribution constants. In many instances, when the determination of H_l presents certain difficulties, it is convenient to employ the percentage content *P* of the SLP in the column as a characteristic:

$$\frac{V_N}{V_{N,st}} = \frac{K_l}{K_{l,st}} + \lambda_2 \frac{1}{P} , \qquad (26)$$

where λ_2 is a constant.

The proposed methods can be used to determine the ratio of the distribution constant to the thermodynamic characteristic of the substance which can be used to identify it. The relative distribution constant is independent of the content of the SLP and of the type of solid carrier.

Together with relative retentions, the system of Kovats indices[34] is used in gas chromatography for the identification of compounds:

$$I = 100z + 100 \cdot \frac{\lg (V_N / V_{Nz})}{\lg (V_{N(z+1)} / V_{Nz})} , \qquad (27)$$

where V_{nz} and $V_{N(z+1)}$ are the corrected retention volumes of n-alkanes whose molecules contain *z* and *z*+1 carbon atoms. This equation can be reduced to equations of the type

$$I = I_0 + \lambda_3 \cdot \frac{1}{H_l} , \qquad (28)$$

$$I = I_0 + \lambda_4 \cdot \frac{1}{P} , \qquad (29)$$

where λ_3 and λ_4 are constants, which are determined by the adsorption interactions of the sorbate in the chromatographic system and by the dimensions of the argument employed; I_0 is an invariant quantity for the determination of which one employs the corresponding relative distribution constants instead of the relative retention volumes, i.e. it is a universal constant:

$$I_0 = 100z + 100 \cdot \frac{\lg (K_l / K_{lz})}{\lg (K_{l(z+1)} / K_{lz})} . \qquad (30)$$

It is desirable to select as standard a substance whose retention is determined solely by dissolution. For non-polar phases and phases of medium polarity, n-alkanes meet the requirements for standard compounds, while in the case of polar SLP it is convenient to select polar compounds (for example, alcohols) as standards. Consequently, in order to identify the compounds analysed, it is essential in the general case to separate from the overall retention volume the contribution due solely to the dissolution of the chromatographed substance in the SLP.

Thus general methods have been proposed for the identification of chromatographed compounds in gas–liquid chromatography,[90] based on the use of invariant characteristics of the retention, independent of adsorption.

We used the methods[46,90] based on the employment of the relation between the relative retentions and the reciprocal of the content of the SLP on the solid carrier to interpret both literature data and our own experimental data. A completely satisfactory agreement between experiment and theory was obtained in all cases.

As an example, Fig.8 presents the relations between the relative retention volume and the reciprocal of the content of the SLP on the solid carrier; experimental data obtained by Pecsok et al.[14] were used to derive these relations. It is seen from Fig.8 that, in conformity with the theory, the graphs for all the substances chromatographed are linear and make the same intercept on the ordinate axis for different solid carriers, which corresponds to the ratio of the distribution constants of the given substance and the standard. The methods

proposed can therefore be used successfully to determine the ratio of the distribution constants – a thermodynamic characteristic of the substance on the basis of which it can in fact be identified. The ratios $K_l/K_{l,st}$ obtained are independent of the content of SLP and of the type of solid carrier. As already mentioned above, the application of the additive theory of retention in capillary chromatography has a number of specific features associated with the need to use the capacity coefficient k_{st} as the characteristic of the content of SLP in the capillary column. Since the Kovats retention indices are at present the most widely used system of retention units in gas chromatography, it appeared essential to test the validity of the following expression for the retention indices in capillary chromatography:[51]

$$I_i = I_{0i} + a_{Ii} \cdot \frac{1}{k_{st}} . \qquad (31)$$

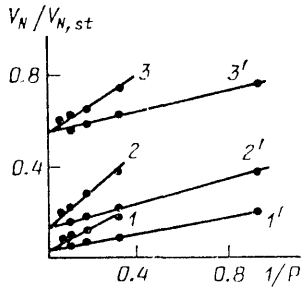


Figure 8. Dependence of the relative retention volume (standard–ethyl methyl ketone) on the reciprocal of the SLP content on the solid carrier (according to the data of Pecsok et al.[14]). Experimental conditions: SLP–ββ'-oxydipropionitrile, temperature 25 °C, solid carrier–Chromosorb W (lines *1'–3'*) and refractory brick (lines *1–3*); compounds: 1) and 1') n-heptane; 2) and 2') butyl ethyl ether; 3) and 3') ethyl acetate.

Using this equation, it is possible to determine the limiting value of the retention index I_{0i}, which depends solely on the solubility of the chromatographed substance in the SLP, and the quantity a_{Ii}, which depends on the adsorption of the chromatographed substance on the interfaces between the SLP and the carrier gas and the solid carrier. Experiments on a capillary column were carried out using different chromatographic systems: gas–polar phase [1,2,3-tris(cyanoethoxy)-propane]–stainless steel, gas–polar phase (Carbowax 20M)–alkaline glass, and gas–non-polar phase (Apiezon L)–alkaline glass. For all the systems indicated and compounds investigated (benzene, *o*-xylene, and *cis*- and *trans*-isomers of pentadecene), it has been shown[95] that Eqn.(31) describes satisfactorily the experimental data (Fig.9).

An important condition for the successful employment of an equation of type (31) is the selection of a system of standards for the retention indices. For the homologous series of compounds employed as standards as well as the compound whose capacity coefficient was used in Eqn.(31), it is useful to choose substances whose properties approach ideality, i.e. whose retention is determined mainly by dissolution and the contribution of adsorption to retention is minimal. The importance of this factor had been demonstrated earlier for packed columns and it has been studied systematically for capillary columns.[95] In the case of a stainless steel column (50 m × 0.25 mm) with 1,2,3-tris(cyanoethoxy) propane as the SLP at 50 °C, $I_{0i} = 1405 \pm 38$ and $a_{Ii} = 245 \pm 54$ (with n-alkanes as standards) or $I_{0i} = 908.3 \pm 2.0$ and $a_{Ii} = -10.4 \pm 4.0$ (with n-alkenes as standards) have been obtained for *o*-xylene. Table 6[95] presents the values of I_{0i} and a_{Ii} obtained for n-pentadecene isomers on Carbowax 20M at 110° on a 50 m × 0.25 mm stainless steel column. Evidently the use of the homologous series of alk-1-enes made it possible to improve the reproducibility of the quantities I_{0i} by a factor of 2–50 and that of the quantities a_{Ii} by a factor of 3–70. 2-Alkyl-1-ethylbenzenes have also been used[95] as standards. However, a better reproducibility of I_{0i} and a_{Ii} was achieved using as standards alk-1-enes, i.e. compounds whose chemical properties are closest to those of the compounds investigated.[33]

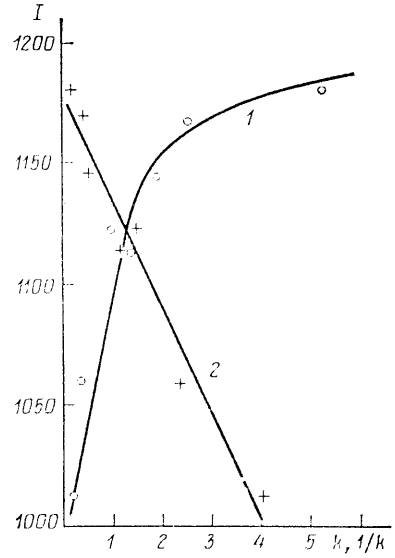


Figure 9. Dependence of the retention index of benzene (standards–n-alkanes) on the capacity coefficient (curve *1*) and on its reciprocal (curve *2*).[95] Experimental conditions: 50 m × 0.25 mm stainless steel columns, SLP–tris(cyanoethoxy) propane, temperature 50 °C.

The analysis of n-alkenes (for example, pentadec-1-ene) on a non-polar phase (Apiezon L) at 164 °C using compounds in the homologous series of n-alkanes as standards yielded $I_{0i} = 1489.6 \pm 1.0$ and $a_{Ii} = -0.38$.

A rational choice of the homologous series of compounds to be used as standards for the system of Kovats indices significantly improves the reproducibility of the latter for the compounds chromatographed and the reproducibility of the limiting value of I_{0i}. Thus, instead of the usually employed retention index I, the quantity I_{0i} can be usefully employed for the identification of compounds on the basis of chromatographic data; this quantity should in fact be used in tables bearing in mind its better reproducibility in experiments in different laboratories.

The differences between the retention characteristics of hydrocarbons as a function of their type (for example, the *cis*- or *trans*-isomers of alkenes) on columns with different SLP contents can be employed in gas–liquid–solid chromatography for the identification of the compounds analysed. This assumption was first made in a study[51] where it was shown that the relative retentions of n-paraffins and aromatic hydrocarbons vary unequally as the column ages, which can

be employed for the identification of these classes of compounds.

Indeed, if the retention of compounds analysed is determined by two groups of phenomena—the dissolution in the SLP and adsorption at the SLP interfaces, then, following a change in the SLP content, one in fact obtains a new column with new chromatographic properties, which is equivalent to the employment of a new phase. In analysing this phenomenon, one should note that, in conformity with the available data (see, for example, Berezkin et al.[92]), the contribution of adsorption to retention is unique as regards the chromatographic separation effects attained and can be particularly usefully employed in the separation of isomeric compounds. Therefore, using jointly dissolution and adsorption, it is possible in many instances to improve the separation and, when two and more columns are employed, it is possible to achieve the group identification of compounds.

Table 6. The invariant values of the retention index I_{0i} and the adsorption parameter a_{Ii} and the corresponding standard deviations s for n-pentadecene isomers [calculation by Eqn. (31)].[95]

n-Pentadecene isomers	Standards—n-alkanes				Standards—alk-1-enes			
	I_{0i}	s	a_{Ii}	s	I_{0i}	s	a_{Ii}	s
cis-Pentadec-7-ene	1525.4	3.0	−41.7	1.3	1476.8	1.7	1.9	0.74
cis-Pentadec-6-ene	1528.5	2.9	−42.1	1.3	1480.4	1.6	1.2	0.72
cis-Pentadec-5-ene	1533.7	4.8	−43.5	2.2	1485.9	0.2	−0.2	0.1
cis-Pentadec-4-ene	1539.9	5.4	−44.5	2.4	1491.9	0.5	−0.7	0.2
cis-Pentadec-3-ene	1548.4	5.9	−46.0	2.4	1500.5	0.1	−1.1	0.2
cis-Pentadec-2-ene	1576.4	7.2	−23.6	4.9	1529.6	2.2	−7.4	1.2
trans-Pentadec-7-ene	1526.2	3.6	−9.6	1.6	1477.9	1.1	3.8	0.5
trans-Pentadec-6-ene	1528.2	3.5	−9.7	1.6	1479.6	1.0	3.0	0.5
trans-Pentadec-5-ene	1531.1	3.5	−10.4	1.6	1482.8	1.1	3.0	0.5
trans-Pantadec-4-ene	1533.0	3.8	−11.1	1.7	1484.6	0.9	3.0	0.4
trans-Pentadec-3-ene	1542.6	4.9	−13.6	2.4	1494.1	0.1	1.8	0.1
trans-Pentadec-2-ene	1562.2	6.4	−25.4	3.4	1514.7	1.7	−2.7	0.8
Pentadec-1-ene	1547.9	5.0	−14.7	2.5	—	—	—	—

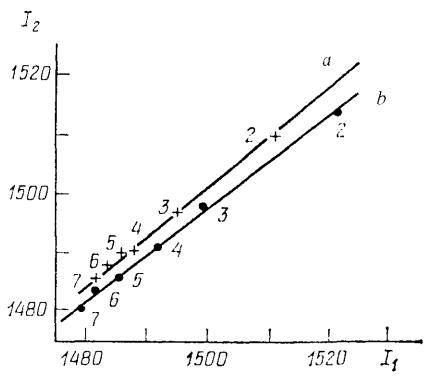


Figure 10. Relation between the retention indices for the *cis*- and *trans*-isomers of pentadecene on Carbowax 20M at 110 °C on two glass columns differing in the effective thickness of the SLP film;[51] I_1 and I_2 are the retention indices of the compound on columns *1* and *2* respectively; the thickness of the SLP layer on column *2* is twice as great as on column *1*: *a*) relation for the *trans*-isomers of pentadecene; *b*) relation for the *cis*-isomers of pentadecene; the numerals opposite the points denote the position of the double bond in the pentadecene isomer.

Fig. 10 presents data obtained on glass columns[51] differing only in the SLP content (the thickness of the SLP film on the second column was approximately twice as great as on the first). The use of data obtained on these two columns makes it possible to trace clearly two linear relations for the *cis*- and *trans*-isomers of pentadecene, which can be used for identification. We may note that relations of this type had been employed earlier solely for columns with different SLP.[96] In order to enhance the role of the adsorption factor, it may be that in the future it will prove desirable to employ one of the following procedures: (1) to increase the surface area of the walls of capillary columns and to subject them to extensive special treatment (for example, etching, deposition of a porous layer, etc); (2) to introduce specially into the SLP a small amount of a finely dispersed solid adsorbent. New possibilities for identification can be particularly usefully employed in capillary chromatography bearing in mind the selectivity and accuracy of the measurements of the retention characteristics.

VI. THE ROLE OF ADSORPTION PHENOMENA IN THE AGEING OF CAPILLARY COLUMNS

An important problem in capillary chromatography is the time variation of the properties of capillary columns (ageing), which has a negative influence on almost all the chromatographic properties of the columns (efficiency, separation, symmetry of chromatographic bands, reproducibility, retention characteristics, etc.). The ageing of packed columns was investigated long ago (see, for example, Dal Nogare and Juvet[16]): different investigators put forward the following main causes of the time variation of the properties of packed columns during their use: (1) the volatilisation of the stationary liquid phase from the columns;[16,97] (2) the redistribution of the SLP on the sorbent;[98,99] (3) the variation of the properties of the SLP as a result of its decomposition or oxidation by admixtures of oxygen in the carrier gas.[100]

The ageing of columns in capillary chromatography has not been studied in detail, although a number of hypotheses have been put forward concerning its nature.[87] Thus, according to Schomburg et al.,[101] one of the main causes of ageing is the transition from a continuous homogeneous film of SLP to a coating on the internal walls of the columns made up of isolated droplets. In a study specially devoted to the problem of ageing of capillary columns,[51] the hypothesis was put forward that the ageing process is associated mainly with the volatilisation of part of the SLP from the column. Jennings pointed out in a monograph[87] the great importance of the problem of the ageing of capillary columns in connection with the increase of their useful life.

Ageing has been studied on stainless steel columns (50 m × 0.25 mm) with 1,2,3-tris(cyanoethoxy)propane (TCEP) as the SLP. The changes in the properties of the columns were investigated at 130 °C in a stream of nitrogen (the pressure at the inlet to the column was 2.0 atm). The ageing of the columns was assessed from the change in the retention index I and the capacity coefficient k for benzene; I and k were measured at 50 °C and a nitrogen pressure at the inlet to the column of 0.6 atm. The maximum permissible working temperature for TCEP is 150–160 °C.[87,103]

In the first place it is essential to note that ageing influences not only the retention characteristics but also the separating capacity of the capillary column. Fig. 11[102] presents two chromatograms obtained on an ageing column over a period of two weeks. As a result of ageing for two weeks, two pairs of hydrocarbons, which were satisfactorily separated on a freshly prepared column, virtually ceased to

separate. The above example demonstrates the significant influence of ageing and the importance of studying its causes.

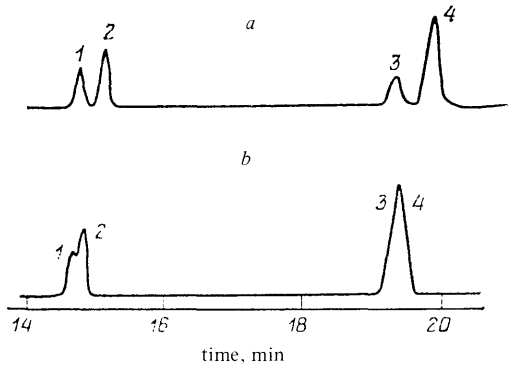


Figure 11. Variation of the separation during the ageing of the capillary column:[102] *a*) separation on a freshly prepared column; *b*) separation on the same column after ageing for 2 weeks. Experimental conditions: column length 50 m; SLP–tris(cyanoethoxy)propane; ageing temperature 130 °C; temperature of the measurement of the chromatographic characteristics 94 °C; compounds: 1) n-tetradecane (C_{14}); 2) 1-ethyl-4-methylbenzene; 3) n-pentadecane (C_{15}); 4) 1-methyl-2-propylbenzene.

The results of the variation of the quantities I and k for benzene as a function of the duration of ageing on capillary columns at 130 °C are presented in Fig.12.[102] The retention index and the capacity coefficient were measured at 50 °C.

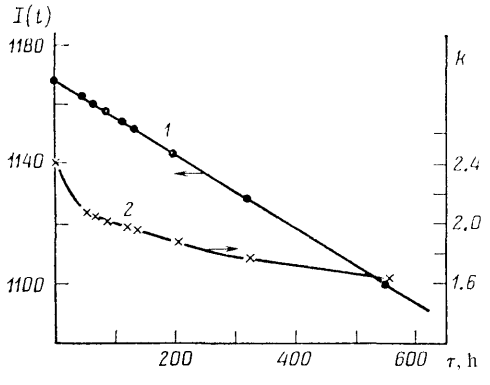


Figure 12. Variation of the retention index I (line *1*) and the capacity coefficient k (line *2*) for benzene as a function of the duration of ageing τ of a capillary column with tris(cyanoethoxy)propane at 130 °C.[102]

Independent experiments have shown that the variation of the chromatographic properties of open capillary columns for small carrier gas pressure drops in the column is associated mainly with the volatilisation of the SLP in the initial sections of the column. Thus, a small initial section consists of a column with a very thin layer of SLP. The separation in the initial (first) column is due mainly to adsorption processes. Therefore an ageing capillary column can be regarded to a first approximation as a compound column. Using the theory of retention on compound columns,[104] the following equation has been obtained:[102]

$$I(t) = I(0) - dt, \qquad (32)$$

where $I(t)$ is the retention index of the test substance at time t, t the ageing time, d a constant, and $I(0)$ the retention index in the initial instant. This equation describes experimental data satisfactorily (Fig.12).

In order to increase stability, it is useful to employ the SLP in capillary columns at a temperature 50 °C below that recommended for packed columns. It is recommended that a carrier gas fully or partly saturated by the vapour of the SLP employed be used at elevated temperatures in order to increase the lifetime of capillary columns. A device proposed recently is useful for the realisation of this recommendation.[105]

VII. THE INFLUENCE OF ADSORPTION PHENOMENA ON THE SPREADING OF CHROMATOGRAPHIC BANDS IN GAS–LIQUID CAPILLARY CHROMATOGRAPHY

The first studies on the theory of the efficiency of capillary chromatographic columns were the familiar investigations by Golay,[107,108] which have still not lost their importance even at the present time. A straight capillary column with a circular or slit-like cross-section and smooth walls coated by a thin layer of SLP was considered in these studies. Golay obtained an expression for the HETP in the cases indicated. The influence of the finite rate of diffusion within the SLP film was taken into account approximately with the aid of an equivalent electrical circuit for the retaining layer.[109,110] In subsequent studies by Golay[111–114] the above theory was developed in several directions. Following the introduction of capillary columns with a porous layer, Golay modified his equation and extended it to such columns.[111] A detailed investigation of this equation was described subsequently.[115] Golay[112] considered a flow of the Poiseuille type in a bent column and showed that, under the conditions of the Poiseuille type in such a column, the operation of centrifugal forces creates a "secondary flow", which decreases the HETP. An expression has been obtained[113] for the dynamic diffusion coefficient, which plays a significant role in the spreading of the chromatographic band in capillary chromatography in columns (tubes) with an elliptical cross-section. Golay[114] considered the question of the magnitude of this coefficient for tubes with an extended rectangular cross-section.

In a series of communications, Giddings[116–120] considered in general terms the processes occurring in chromatographic capillary columns; using the approximate principle of additivity, the author estimated the contributions of different mechanisms leading to the spreading of the chromatographic band.

The influence of various types of mass transfer in gas–liquid capillary chromatography was estimated approximately in the book of Zhukhovitskii and Turkel'taub.[20]

A mathematically more rigorous study of the chromatographic band in a capillary column, compared with the work of Golay and Giddings, has been carried out by Khan[121] using the method of moments; it took into account the effect of the finite rate of mass transfer through the gas phase–liquid phase interface (see also another communication by the same author[122]).

The expression obtained by Golay for the height equivalent to a theoretical plate H in the case of a capillary column having a circular cross-section with a radius r_0 is

$$H = \frac{2D_g}{u} + \left[\frac{(1+6k+11k^2)}{24(1+k)^2}\frac{r_0^2}{D_g} + \frac{2}{3}\frac{k}{(1+k)^2}\cdot\frac{\delta^2}{D_l}\right]u \cdot \qquad (33)$$

For a column having a slit-like cross-section with a slit width $2h$, this expression is somewhat modified:

$$H = \frac{2D_g}{u} + \left[\frac{4}{105}\cdot\frac{(1+9k+25.5k^2)}{(1+k)^2}\frac{h^2}{D_g} + \frac{2}{3}\cdot\frac{k}{(1+k)^2}\frac{\delta^2}{D_l}\right]u \quad (34)$$

where D_g and D_l are the diffusion coefficients of the chromatographed substance in the gas and liquid phases and δ is the thickness of the SLP film.

The first (identical) terms in Eqns.(33) and (34) describe the effect of longitudinal diffusion in the gas phase, while the second terms are due to the phenomenon of dynamic diffusion arising from the fact that in the capillary column there is a distribution of the flow rate with respect to the radius. The last term, which is also identical for the columns of the forms considered, is associated with the effect of diffusion within the SLP film.

A more general expression for the HETP, obtained by Khan,[121,122] includes an additional term:

$$H_M = \frac{2k}{(1+k)^2}\cdot\frac{\delta}{k_d}, \quad (35)$$

where k_d is the rate constant for the desorption of the test substance from the gas phase–liquid phase interface. This term reflects the effect of the additional resistance to mass transfer at the gas–liquid boundary associated with the finite rate of attainment of equilibrium at this boundary. However, it has been shown[123] that the above term does not usually make an appreciable contribution to the spreading of the chromatographic peak in gas–liquid capillary chromatography.

As in gas–liquid chromatography on packed columns,[32,124,125] allowance for the influence of adsorption phenomena on such a spreading process appears much more significant in this instance. In this connection mention should be made of a study[126] in which the theory of the spreading of peaks in a capillary column proposed by Golay was tested and the occurrence of peak spreading not taken into account by Golay's theory was demonstrated. This spreading is associated with the mass transfer in the stationary phase but is independent of the thickness of the liquid film. The authors[126] believe that it is caused by the adsorption of the substances analysed from the stationary liquid phase on the walls of the nylon capillary.

It therefore appears useful to discuss briefly a theoretical model of the chromatographic process in a capillary column taking into account the adsorption at the gas–SLP and SLP–solid wall interfaces. In order to obtain the principal characteristics of the chromatographic elution curve, we shall employ the method of static moments which is nowadays widely used in the theory of chromatography [see, for example, Zolotarev's review[127]]. The approach described below has been proposed by Zolotarev et al.[128]

We shall consider initially a straight cylindrical column with a circular cross-section. Suppose that $c_g^*(x,r,t)$ is the local concentration of the chromatographed substance in the gas phase. Then, if the distribution of the local velocity $v(r)$ in the gas along the tube cross-section is parabolic, the local differential equation of mass transfer in the capillary column can be formulated as follows:

$$D_g\left(\frac{\partial^2 c_g^*}{\partial r^2} + \frac{1}{r}\frac{\partial c_g^*}{\partial r} + \frac{\partial^2 c_g^*}{\partial x^2}\right) - v(r)\frac{\partial c_g^*}{\partial x} - \frac{\partial c_g^*}{\partial t} = 0,$$
$$v(r) = 2u\left(1 - \frac{r^2}{r_0^2}\right), \quad (36)$$

where x is the coordinate along the column axis, r the radial coordinate reckoned from the centre of the column, t the time, u the carrier gas flow rate averaged with respect to the cross-section, and r_0 the radial coordinate of the boundary of the free part of the column (Fig.1). Eqn.(36) represents the mass balance of the chromatographic impurity in a small volume element at a distance r ($r<r_0$) from the column axis. The mass balance condition should hold at the gas–SLP ($r = r_0$) interface: the diffusion flux of the impurity across this interface should be equal to the sum of the rates of change of the masses of the impurity in the liquid phase and in the adsorbed states at the interfaces:

$$\gamma_l\frac{\partial a_l}{\partial t} + \gamma_{gl}\frac{\partial a_{gl}}{\partial t} + \gamma_{ls}\frac{\partial a_{ls}}{\partial t} = -\frac{2\gamma_g D_g}{r_0}\cdot\left.\frac{\partial c_g^*}{\partial r}\right|_{r=r_0}. \quad (37)$$

We shall average Eqn.(36) with respect to the free volume of the column. For this purpose, we shall apply to each term of Eqn.(36) the averaging operator with respect to the cross-section and we shall take into account Eqn.(37). We then obtain

$$\gamma_l\frac{\partial a_l}{\partial t} + \gamma_g\frac{\partial c_g}{\partial t} + \gamma_{gl}\frac{\partial a_{gl}}{\partial t} + \gamma_{ls}\frac{\partial a_{ls}}{\partial t} =$$
$$= \gamma_g D_g\frac{\partial^2 c_g}{\partial x^2} - 4\gamma_g\frac{u}{r_0^2}\int_0^{r_0}\frac{\partial c_g^*}{\partial x}\left(1 - \frac{r^2}{r_0^2}\right)r\,dr, \quad (38)$$

where $c_g(x,t)$ and $a_l(x,t)$ are the average concentrations of the chromatographed impurity in the mobile phase and in the SLP. The local concentration of the impurity in the SLP will be designated by $a_l^*(x,y,t)$.

We shall assume as usual that the SLP is thin ($\delta \ll r_0$). For such a thin film, we have

$$\gamma_l + \gamma_g = 1;\ \gamma_g = \frac{r_0^2}{(r_0+\delta)^2} \simeq 1 - \frac{2\delta}{r_0};\ \gamma_l \simeq \frac{2\delta}{r_0^2};\ \gamma_{gl} \simeq \gamma_{ls} \simeq \frac{\gamma_l}{\delta}. \quad (39)$$

We shall assume that the equilibrium at the interfaces is established at an infinitely high rate. The following equilibrium relation between the local concentrations of the impurity in the gas and liquid phases will then hold at the gas–SLP interface:

$$(a_l^*)_i = K_l(c_g^*)_i, \quad (40)$$

where K_l is the partition coefficient between the gas and liquid phases and the subscript i refers to this interface. In addition, assuming that the gas adsorption isotherm is linear with a Henry coefficient K_{gl}, we have at the above interface

$$a_{gl} = K_{gl}(c_g^*)_i. \quad (41)$$

The diffusion of the impurity in the thin SLP film ($\delta \ll r_0$) can be described by the one-dimensional equation for diffusion along the coordinate y at right angles to the film boundaries (Fig.1):

$$\frac{\partial a_l^*}{\partial t} = D_l\frac{\partial^2 a_l^*}{\partial y^2};\ a_l(x,t) = \frac{1}{\delta}\int_0^{\delta} a_l^*(x,y,t)\,dy;\ 0 \leqslant y \leqslant \delta. \quad (42)$$

At the $y = 0$ (solid wall) boundary and at $y = \delta$ we also obtain the following relations in the case under consideration:

$$a_{ls} = K_{ls}a_l^*|_{y=0};\ \frac{\partial a_{ls}}{\partial t} = D_l\left.\frac{\partial a_l^*}{\partial y}\right|_{y=0};\ a_l^*|_{y=\delta} = (a_l^*)_i. \quad (43)$$

The first of these relations takes into account the adsorption at the SLP–solid interface in terms of the linear isotherm approximation, while the second represents the local mass balance equation at this interface with allowance for adsorption. On solving Eqn.(42) with the aid of the Laplace transformation with respect to time,[129] we obtain the following expression for the representation $\tilde{a}_l = \int_0^{\infty} e^{-st}a_l^* dt$:

$$\tilde{a}_l^* = \frac{(\tilde{a}_l^*)_i[\sinh(\varkappa y) + (D_l\varkappa/K_{ls}s)\cosh(\varkappa y)]}{\sinh(\varkappa\delta) + (D_l\varkappa/K_{ls}s)\cosh(\varkappa\delta)};\ \varkappa = \left(\frac{s}{D_l}\right)^{1/2}. \quad (44)$$

Application of the Laplace transformation to Eqn.(43) and substitution of Eqn.(44) for $\tilde{a}_l^*$ yields after simple rearrangements

$$(\tilde{a}_l^*)_i = P_1(s)\,\tilde{a}_l$$

$$P_1(s) = \frac{(\varkappa\delta)\{\sinh(\varkappa\delta) + [1/(\varkappa K_{ls})]\cosh(\varkappa\delta)\}}{\{\cosh(\varkappa\delta) + [1/(\varkappa K_{ls})]\sinh(\varkappa\delta) - 1\}} \quad . \tag{45}$$

Using Eqns.(43)–(45), we find the following formula for a_{ls}:

$$\tilde{a}_{ls} = P_2(s)\cdot\tilde{a}_l$$

$$P_2(s) = \frac{\delta}{\cosh(\varkappa\delta) + [1/(\varkappa K_{ls})]\sinh(\varkappa\delta) - 1} \quad . \tag{46}$$

Taking into account the boundary conditions (40) and (41) and also Eqn.(45), we obtain

$$\tilde{a}_{gl} = (K_{gl}/K_l)\,P_1(s)\,\tilde{a}_l \quad . \tag{47}$$

For subsequent treatment, we express[107,108,121] the local concentration of the test substance in the gas phase c_g^* by the equation

$$c_g^* = c_g + \Delta c_g;\ \int_0^{r_0} \Delta c r\,\mathrm{d}\,r = 0 \quad . \tag{48}$$

In addition we assume that the relation

$$\Delta c \ll c_g \tag{49}$$

holds.

Then, substituting Eqn.(48) in Eqns.(36) and (38), and taking into account formula (49), we obtain the following equation for Δc after a few steps which we omit here:

$$\frac{\partial^2\Delta c}{\partial r^2} + \frac{1}{r}\frac{\partial\Delta c}{\partial r} = \frac{u}{D_g}\left(1 - 2\frac{r^2}{r_0^2}\right)\frac{\partial c}{\partial x} - \\ - \frac{\chi_l}{D_g\chi_g}\frac{\partial a_l}{\partial t} - \frac{\chi_{gl}}{\chi_g D_g}\cdot\frac{\partial a_{gl}}{\partial t} - \frac{\chi_{ls}}{\chi_g D_g}\cdot\frac{\partial a_{ls}}{\partial t} \quad . \tag{50}$$

On solving this equation taking into account condition (45) and the requirement that Δc be finite at $r \to 0$, we find

$$c_g^* = c_g + \frac{u}{D_g}\left(\frac{r^2}{4} - \frac{r^4}{8r_0^2} - \frac{r_0^2}{12}\right)\frac{\partial c_g}{\partial x} - \\ - \frac{\chi_l}{D_g\chi_g}\left(\frac{r^2}{4} - \frac{r_0^2}{8}\right)\left(\frac{\partial a_l}{\partial t} + \frac{\chi_{gl}}{\chi_l}\frac{\partial a_{gl}}{\partial t} + \frac{\chi_{ls}}{\chi_l}\frac{\partial a_{ls}}{\partial t}\right) \quad . \tag{51}$$

Application of the Laplace transformation to Eqn.(51) at the gas–SLP interface taking into account Eqns.(40) and (41) yields

$$(\tilde{c}_g^*)_i = \frac{(\tilde{a}_l^*)_i}{K_l} = \frac{P_1(s)}{K_l}\,\tilde{a}_l = \tilde{c}_g + \frac{ur_0^2}{24D_g}\frac{\mathrm{d}\,\tilde{c}_g}{\mathrm{d}\,x} - \frac{r_0^2 s}{8D_g}\frac{\chi_l}{\chi_g} \times \\ \times\left(\tilde{a}_l + \frac{\chi_{gl}}{\chi_l}a_{gl} + \frac{\chi_{ls}}{\chi_l}a_{ls}\right) \quad . \tag{52}$$

On substituting Eqns.(44)–(46) in Eqn.(52) and on solving the resulting expression for $\tilde{a}_l$, we find

$$\tilde{a}_l = K_l\left[P_1(s) + \frac{r_0^2 s}{8D_g}k\left(1 + \frac{\chi_{gl}K_{gl}}{\chi_l K_l}P_1(s) + \frac{\chi_{ls}P_2(s)}{\chi_l}\right)\right]^{-1} \times \\ \times\left(\tilde{c}_g + \frac{ur_0^2}{24D_g}\cdot\frac{\mathrm{d}\,c_g}{\mathrm{d}\,x}\right), \\ k = \chi_l K_l/\chi_g. \tag{53}$$

We now differentiate Eqn.(53) with respect to x and substitute the resulting expression in Eqn.(47). After integration and subsequent application of the Laplace transformation taking into account Eqns.(44)–(46) and (53), we obtain the following expression for $\tilde{c}_g$:

$$B\frac{\mathrm{d}^2\tilde{c}}{d\,x^2} - \frac{\mathrm{d}\tilde{c}_g}{\mathrm{d}\,x} - E\tilde{c}_g = 0 \ , \\ B = \frac{1}{u\theta}\left\{\left(D_g + \frac{u^2r_0^2}{48D_g}\right)\left[P_1(s) + \frac{r_0^2 s}{8D_g}kQ(s) - ksQ(s)\left(\frac{ur_0^2}{24D_g}\right)^2\right]\right\}, \\ E = \frac{1}{u\theta}\left\{s\left[P_1(s) + \frac{r_0^2}{8D_g}skQ(s) + ksQ(s)\right]\right\} \ , \tag{54}$$

$$\theta = P_1(s) + \frac{sr_0^2}{24D_g}ksQ(s) \ ,$$

$$Q(s) = 1 + \frac{\chi_{gl}K_{gl}P_1(s)}{K_l\chi_l} + \frac{\chi_{ls}P_2(s)}{\chi_l} \quad .$$

We shall assume that the impurities are introduced into the column in the form of a rectangular pulse of duration ε:

$$x = 0 \quad \begin{cases} c_g = c_0, & 0 < t \leqslant \varepsilon \\ c_g = 0, & t > \varepsilon \end{cases} \tag{55}$$

Accordingly, we have the following boundary conditions for Eqn.(54):

$$\tilde{c}_g = \frac{c_0}{s}(1 - \mathrm{e}^{-\varepsilon s}),\ x = 0 \ , \tag{56}$$

where $\tilde{c}_g$ is finite at $x \to \infty$.

The solution of Eqn.(52) subject to conditions (54) is

$$\frac{\tilde{c}_g(L, s)}{\varepsilon c_0} = \left(1 - \frac{\varepsilon s}{2!} + \frac{\varepsilon^2 s^2}{3!} - \cdots\right)\exp\left\{\frac{L}{2B}[1 - (1 + 4BE)^{1/2}]\right\}, \tag{57}$$

where $x = L$ is the distance from the beginning of the column at which the chromatographic elution curve is measured.

We apply the familiar methods for the calculation of the moments of the elution curve from its representation[129,130] and then, using Eqns.(57) and (54), we obtain

$$m_1(L) = \int_0^\infty \frac{c_g(L, t)}{\varepsilon c_0}\,t\,\mathrm{d}\,t = -\lim_{s\to 0}\frac{\mathrm{d}}{\mathrm{d}\,s}\left[\frac{\tilde{c}_g(L, s)}{\varepsilon c_0}\right] = \frac{\varepsilon}{2} + \frac{L}{u}(1 + k_*), \tag{58}$$

$$m_2(L) = \int_0^\infty \frac{c_g(L, t)}{\varepsilon c_0}\,t^2\,\mathrm{d}\,t = \lim_{s\to 0}\frac{\mathrm{d}^2}{\mathrm{d}\,s^2}\left[\frac{\tilde{c}_g(L, s)}{\varepsilon c_0}\right] = \frac{\varepsilon^2}{12} + \left[\frac{\varepsilon}{2} + \frac{L}{u}(1 + k_*)\right]^2 + \\ + \frac{L}{u^2}(1 + k_*)^2\left[\frac{2D_g}{u} + \frac{ur_0^2}{D_g}\frac{(1 + 6k_* + 11k_*^2)}{24(1 + k_*)^2} + \frac{2}{3}\frac{uk_*}{(1 + k_*)^2}\frac{\delta^2}{D_l}f_1(K_{gl}, K_{ls})\right], \tag{59}$$

$$f_1 = \frac{\delta^2 + 3K_{ls}\delta + 2K_{ls}^2}{\delta^2 + K_{gl}\delta/K_l + K_{ls}\delta};\quad k_* = \frac{\chi_l}{\chi_g}K_l\left(1 + \frac{K_{gl}/K_l + K_{ls}}{\delta}\right). \tag{60}$$

Here

$$m_k(x) = \int_0^\infty t^k c_g(x, t)\,\mathrm{d}\,t \Big/ \int_0^\infty c_g(x, t)\,\mathrm{d}\,t$$

is the initial moment of the kth order chromatographic elution curve.

In order to obtain, in particular, the HETP, we make use of the relation

$$H = L\mu_2^{(0)}/(m_1^{(0)})^2,\ \mu_2^{(0)} = m_2^{(0)} - [m_1^{(0)}]^2 \ , \tag{61}$$

where $m_1^{(0)}(x)$, $m_2^{(0)}(x)$, and $\mu_2^{(0)}(x)$ are the first and second initial moments and the second central moment of the chromatographic curve for a sample volume tending to zero ($\varepsilon \to 0$).

Taking into account Eqns.(54)–(57), we obtain the following formula for the HETP:

$$H = \frac{2D_g}{u} + \frac{1 + 6k_* + 11k_*^2}{24(1 + k_*)^2}\frac{ur_0^2}{D_g} + \frac{2}{3}\frac{uk_*}{(1 + k_*)^2}\frac{\delta^2}{D_l}f_1(\delta, K_{gl}, K_{ls}). \tag{62}$$

The expression for the HETP in a column with a slit-like cross-section can be readily obtained with the aid of the method used above for the evaluation of the moments and the HETP for a cylindrical column. Here the term describing the internal diffusion for the thin SLP films considered ($\delta \ll r_0$, $\delta \ll h$) will be the same as for a cylindrical column. For a column with a rectangular cross-section, the expression for the HETP is

$$H = \frac{2D_g}{u} + \frac{4}{105}\cdot\frac{(1 + 9k_* + 25.5k_*^2)}{(1 + k_*)^2}\cdot\frac{uh^2}{D_g} + \frac{2}{3}\frac{uk_*}{(1 + k_*)^2}\cdot\frac{\delta}{D_l}f_1(\delta, K_{gl}, K_{ls}) \tag{63}$$

It is evident from the expressions obtained that adsorption at the gas–SLP and SLP–solid interfaces influences H in two ways. Firstly, the capacity coefficient k changes (increases):

$$k_* = k\left(1 + \frac{K_{gl}/K_l + K_{ls}}{\delta}\right), \quad (64)$$

as already stated in previous Sections. Secondly, an additional multiplier appears in the component of H taking into account the contribution of the internal diffusion resistance to mass transfer:

$$f_1(\delta, K_{gl}, K_{ls}) = \frac{\delta^2 + 3K_{ls}\delta + 3K_{ls}^2}{\delta^2 + (K_{gl}/K_l)\delta + K_{ls}\delta}, \quad (65)$$

whose magnitude is greater than unity and which takes into account the adsorption phenomena.

The contribution of adsorption phenomena at the interfaces to the spreading, i.e. to the HETP, can be taken into account also within the framework of the approximate approach developed by Giddings[118] (see also Garbuzov et al.[131]). However, the above approximate approach does not permit the estimation of the contribution of adsorption phenomena to the moments of the chromatographic elution curve of an order higher than the second; the higher order moments characterise the degree of asymmetry of this curve, its steepness, etc. The above treatment allows this. As an example, we shall write the formula for the asymmetry coefficient

$$\gamma = \mu_3^{(0)}/[\mu_2^{(0)}]^{3/2}$$

($\mu_3^{(0)}$ is the third central moment of the elution curve) for the chromatographic elution curve:

$$\gamma = \left[\frac{2D_g L(1+k_*)^2}{u^3} + \frac{r_0 L}{D_g u}(1 + 6k_* + 11k_*^2) + \frac{2}{3}\frac{k_*}{u}\frac{\delta^2}{D_l} f_1\right]^{-3/2} \times$$

$$\times \left[\frac{12D_g^2 L(1+k_*)^2}{u^5} + 4k_*(1+k_*)\frac{D_g L}{D_l u^3}\cdot\delta^2 f_1 + \frac{r_0^2 L}{2u^3}(1 + 6k_* + 12k_*^2 + 7k_*^3) + \right.$$

$$\left. + 2k_*\frac{\delta^2 L}{D_l^2 u} f_2 + \frac{r_0^2 L}{12 D_g u}\frac{\delta^2}{D_l} k_*(3 + 11k_*) f_1 + \frac{3}{(24)^2}\frac{r_0^4 L}{u D_g^2}(1 + 11k_* + 45k_*^2 + 65k_*^3)\right], \quad (66)$$

where

$$f_2(\delta, K_{gl}, K_{ls}) = f_1(\delta, K_{gl}, K_{ls})\left(\delta K_{ls} + \frac{\delta^3}{3}\right) + \frac{\delta^4}{15\left(\delta^2 + \frac{K_{gl}\delta}{K_l} + K_{ls}\delta\right)}. \quad (67)$$

Golay's Eqns.(33) and (34) and their extended forms taking into account adsorption phenomena [Eqns.(62) and (63)] are valid only for short sections of the column, because the absence of a pressure drop and the constancy of the carrier gas flow rate along the column length were assumed in their derivation. Furthermore, in these equations no account is taken of the additional contribution of the spreading outside the column to H, which is[132] a quadratic function of the gas flow rate:

$$H_0 = [\sigma_0^2/L(1+k)^2]u^2, \quad (68)$$

where σ_0 is the variance of the peak associated with the spreading outside the column. For real long gas–chromatographic capillary columns, it is necessary to take into account the effect of the compressibility of the gas, which leads to the appearance of corrections for the pressure drop[108,133] (see also Garbuzov et al.[131]).

The terms of Eqns.(33) and (34) and (62) and (63) referring to the gas phase which remain unchanged along the length of the column must be multiplied by the correction factor ψ_g given by

$$\psi_g = \frac{9}{8}\frac{[(p_i/p_0)^4 - 1][(p_i/p_0)^2 - 1]}{[(p_i/p_0)^3 - 1]^2}, \quad (69)$$

where p_i and p_0 are the pressures of the carrier gas at the inlet to and outlet from the column.

For the term taking into account the resistance to mass transfer in the SLP, the correction coefficient has the same form as the factor of James and Martin:

$$j = \frac{3}{2}\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \quad (70)$$

For the term describing the spreading outside the column, the correction for the compressibility of the carrier gas can be shown to be equal to j^2. The procedure involved in the introduction of these corrections, presupposes that the diffusion coefficient in the carrier gas and its linear flow rate correspond to the conditions at the outlet from the column, i.e. that $D_g = D_0$ and $u = u_0$. Introducing the average quantities $\bar{D}_g = D_0 p_0/\bar{p}$ and $\bar{u} = u_0 p_0/\bar{p}$ and bearing in mind that $D_0 = D_g^* p_0$, $\bar{u} = j u_0$, and $\bar{p} = p_0/j$ (D_g^* is the diffusion coefficient of the substance analysed in the carrier gas at a pressure of 1.00 atm), it is possible to obtain the following general equation for the HETP of long cylindrical columns with a circular cross-section taking into account the spreading outside the column:

$$H = \frac{2D_g^* \psi_g}{\bar{p}\bar{u}} + \frac{1 + 6k_* + 11k_*^2}{24(1+k_*)^2}\frac{r_0^2 \psi_l \bar{p}\bar{u}}{D_l} + \frac{2}{3}\frac{k_* f_1(K_{gl}, K_{ls})}{(1+k_*)^2}\frac{\delta^2 u}{D_l} + \frac{r_0^2 u^2}{D_l(1+k_*)^2}. \quad (71)$$

An expression analogous to Eqn.(71) can be obtained also for long columns with a rectangular cross-section.[81] The equation for the HETP for long columns without taking into account the contribution of adsorption phenomena to the internal diffusion resistance can be obtained from Eqn.(71) if one puts $f_1 = 1$ (the modified Golay equation):

$$H = \frac{2D_g^* \psi_g}{\bar{p}\bar{u}} + \frac{1 + 6k_* + 11k_*^2}{24(1+k_*)^2}\frac{r_0^2 \psi_l \bar{p}\bar{u}}{D_l} + \frac{2}{3}\frac{k_* \delta^2 u}{(1+k_*)^2 D_l} + \frac{r_0^2 u^2}{D_l(1+k_*)^2}. \quad (72)$$

It is seen from Eqns.(71) and (72) that the $H(u)$ relation is not hyperbolic in the general case [the last term of Eqn.(71) is a quadratic function of the flow rate]. In addition, in practice the average pressure in the column frequently varies simultaneously with the average flow rate, since the flow rate is regulated by altering either the inlet or outlet pressure (this factor has been noted by Garbuzov and co-workers[131,134]). In connection with the foregoing, the test of Golay's theory undertaken by Hazeldean and Scott and Desta and Goldup[125, 135,136] appears to us to be insufficiently rigorous. This test was based on the statistical analysis of the dependence of the HETP on the average carrier gas flow rate. The coefficients of Golay's equation, found on the assumption that the latter is hyperbolic, were compared[126,135,136] (see also Giddings[147]) with the calculated values.

Another method of testing the theory has been proposed by Garbuzov and co-workers.[131,134] It is based on the analysis of the dependence of the widening of the chromatographic bands (characterised by the square of the width of the peak at the half height level in units of time–b_t^2) for C_{13}–C_{24} n-alkanes on their mass-transfer (capacity) coefficients k. The capillary tubes were made from borosilicate glass. The methylsilicone OU-101 was used as the SLP.

The HETP is related (see, for example Giddings[31] and Rudenko[138]) to the quantity b_t^2 by the expression

$$\bar{H} = b_t^2 \bar{u}^2/[(1+k)^2 L \times 8 \ln 2]. \quad (73)$$

Fig.13[131] presents the dependence of the experimental (curve *1*) and calculated (curve *2*) values of b_t^2 on the coefficient k for C_{13}–C_{20} n-alkanes (column with OU-101; the average linear flow rate of the helium carrier gas was $\bar{u} = 37.14$ cm s^{-1}). The calculation was based on Eqn.(72) without taking into account the last term (the spreading outside the column) and with allowance for Eqn.(73). It is readily seen that the effect of the spreading outside the column is reflected in the graph by the section *FE*, which can be found by extrapolating the extent of the spreading on plots of b_t^2 against k, obtained experimentally and calculated, to $k = 0$. On average, the effect of the spreading outside the column for three flow rates $\bar{u}$ amounted to $b_t^2(0) \approx 0.5c^2$.

A contribution to the spreading of the peak not taken into account by the theory has been discovered[131,134] with the aid of this procedure. In order to elucidate the causes of the band spreading which had not been accounted for, Garbuzov et al.[131] investigated the influence of the nature of the carrier gas on the behaviour of the n-tetracosane chromatographic band in a glass column with the SE-30 SLP (the carrier gases were hydrogen, helium, nitrogen, and argon). The maintenance of an identical average linear flow rate would have required the establishment of different pressure drops in the column and for this reason the average pressure in the column was different for each gas. The discrepancy between the experimental [determined with the aid of Eqn.(73)] and calculated [Eqn.(72) without the last term] values of HETP increases with increase of the molecular weight of the carrier gas. The difference $\Delta H = H_{exp} - H_{calc}$ (Fig.14) is a linear function of the reciprocal of the diffusion coefficient of n-tetracosane in the gases employed at the corresponding average pressures in the column. The discrepancy between the contribution of dynamic diffusion and the observed arrest of the mass transfer in the gas phase can be estimated from the slope of the straight line; it amounts to ~24% of the calculated value [the second term of Eqn.(72)]. According to Garbuzov et al.,[131] the discrepancy is caused by the non-ideality of the geometry of the column, which exerts a fairly powerful influence on the contribution of dynamic diffusion.[109,110,112-114] When the capillary is extended and at the same time twisted into a spiral, the column may acquire an elliptical cross-section. In addition, the different curvatures of the inner surface of the tube should produce inhomogeneity of the thickness of the liquid film along the perimeter of the column cross-section.[139] The mass rate of movement of the test substance in the gas near a wall with a greater sorption capacity is lower than the corresponding rate at a wall with a lower capacity, which should lead to additional band spreading as a result of an increase of the contribution of dynamic diffusion.

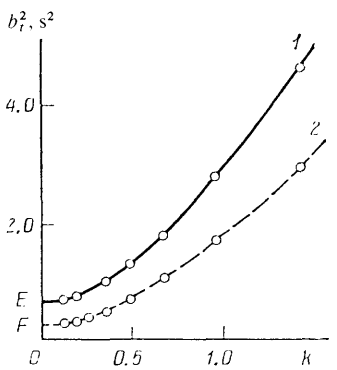


Figure 13. Dependence of the experimental (curve *1*) and calculated (curve *2*) values of b_t^2 on the mass-transfer coefficient k for C_{13}–C_{20} n-alkanes.

The intercept on the ordinate axis made by the straight line in Fig.14 characterises the band spreading which is independent of the nature of the carrier gas. It consists of the contribution to the HETP outside the column, namely $\bar{H}_0 \cong 4.3 \times 10^{-3}$ mm [this contribution is estimated from the quantity $b_t^2(0) \cong 0.5c^2$, which had been found previously by Eqn.(73)], and the contribution of the resistance to the mass transfer in the SLP.

Estimation of the internal diffusion resistance to mass transfer in the SLP film from the third term of Golay's Eqn.(72) using the experimental value $D_l(n\text{-}C_{24}H_{50}$, SE-30, 200 °C) = 2.49×10^{-6} cm²s^{-1} [139] yields a value which is smaller by a factor of 6.5 than that determined from the plot in Fig.(14).

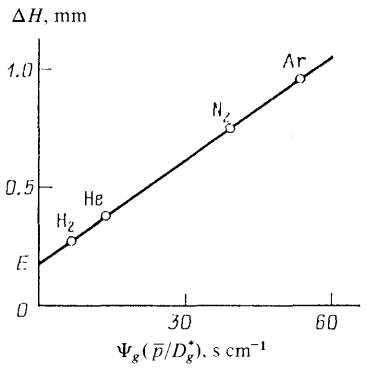


Figure 14. Dependence of the unexplained contribution to the HETP on the reciprocal of the diffusion coefficient of n-tetracosane in various carrier gases at the corresponding average pressures in a column with SE-30.

Garbuzov et al.[131] draw from this finding the entirely justified conclusion that the most probable cause of the above discrepancy is the contribution to the spreading by the adsorption phenomena at the interfaces. They attempted to estimate this contribution using an expression for H_{ads} analogous to the third term in Eqns.(62) and (71); the adsorption of n-tetracosane at the gas–SE-30 interface is then neglected. It is also assumed that the adsorption of n-tetracosane from the SE-30 liquid phase on the solid wall is 200 times less intense than the adsorption of the same substance from the gas on the same wall (the gas–solid distribution constant is known: $K_{gs} \cong 1.242 \times 10^{-4}$ m). Under these conditions, we have $f_1(\delta, K_{gl}, K_{ls}) \cong 6.6$. In other words, it has been shown that even insignificant adsorption of the substance analysed from the liquid phase on the surface of the walls of the capillary column can lead to an appreciable increase of the resistance to mass transfer in the SLP, which also follows from a qualitative model examination of the process.

We may note that we are unaware of studies in capillary chromatography in which the contributions of the adsorption at the SLP interfaces to the column efficiency have been determined rigorously and by a direct experimental method. We believe that such an estimate could be achieved by carrying out two series of experiments on the same column: (1) measurement of the efficiency of a column with adsorption-active walls on which a layer of the SLP has been deposited; (2) measurement of the efficiency of columns with suppressed adsorption activity of the walls. Suppression of adsorption at the SLP–solid interface by modifying the sorbent with small amounts of added polar substances has a positive effect on the efficiency of the preparation of the sorbent. For example, ethyl methyl ketone is eluted in the form of a diffuse band at 50 °C from unmodified Sterchamol impregnated with squalane and the HETP is 11 mm; after modification with 1% triethylene glycol, the HETP falls to 1.6 mm.[140] In the second series of experiments the substances employed to suppress adsorption may be, for example, silanising agents which modify the surface or substances which are not detected by

the flame-ionisation detector and which suppress the adsorption on the active surface centres (for example, ammonia, formamide, formic acid, etc.).

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The development of ideas concerning the role of adsorption has led to the necessity for the refinement of the classification of the types of chromatography based on the state of aggregation of the phases involved in the chromatographic process. The traditional classification considers four main types of chromatography: gas–solid, liquid–solid, gas–liquid, and liquid–liquid.[18] However, the last two types of chromatography are strictly speaking unknown in a pure form, since they cannot be realised without the involvement of a third phase – the solid phase (solid carrier). It is therefore correct to refer to these versions as follows: gas–[liquid–solid] chromatography and liquid–[liquid–solid] chromatography.[32,106]

A rational classification of the types of chromatography which we propose is presented in Table 7. In connection with this classification, it must be emphasised that the gas–liquid chromatography which we have been considering has not so far been realised in the strict sense of its definition and that only gas–[liquid–solid] chromatography has been described. The theoretical ideas concerning the role of adsorption described systematically in this review agree also with the experimental facts obtained in the study of adsorption in capillary columns.

Table 7. Classification of certain common types of chromatography in terms of the state of aggregation of the mobile and stationary phases.

Mobile phase	Stationary phase: solid	Stationary phase: liquid–solid	
		proposed terminology	traditional terminology
Gas	gas[solid]-phase chromatography	gas[liquid–solid]-phase chromatography	gas–liquid chromatography
Liquid	liquid[solid]-phase chromatography	liquid[liquid–solid]-phase chromatography	liquid–liquid chromatography

In conclusion we may note that the new ideas about the role of adsorption in GLC have led to a significant development of the familiar trends in chromatography and the appearance of new ones. A considerable expansion of the applications and an increase of the accuracy of the chromatographic methods for the investigation of the interactions of dissolved compounds with the SLP have been achieved as a result of allowance for the adsorption of the chromatographic substances at the interfaces. The gas-chromatographic study of the adsorption of volatile compounds at the interfaces between the SLP and the solid carrier and the carrier gas has begun to develop (a new physicochemical application of gas chromatography). New ideas and new universal methods for the identification of the chromatographic bands, taking into account the adsorption phenomena in GLC, have been developed. A new classification of the types of chromatography, taking into account the role of the solid carrier (the solid) is proposed.

We may note that the development of capillary gas–[liquid–solid] chromatography is being vigorously continued also at the present time. There is no doubt that in the immediate future the efforts of many investigators will lead to a more complete understanding of the role of adsorption processes in capillary chromatography and to the development of new effective methods for chromatographic separation and physicochemical measurements.

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Institute of Petrochemical
Synthesis,
USSR Academy of Sciences,
Moscow.

Russian Chemical Reviews

December 1984

Translated from *Uspekhi Khimii*, 53, 1929-1958 (1984)

U.D.C. 543.422.27:615.332.017:615.277.3.015.407

Free-radical Mechanisms in the Cytotoxic Action of Antitumour Antibiotics

N.M.Emanuel', G.N.Bogdanov, and V.S.Orlov

The results of studies of the free-radical mechanisms of the action of various antitumour antibiotics are surveyed. The data obtained in the investigation by physicochemical methods (EPR, polarographic, and spectrophotometric) as well as quantum-chemical calculations of the biotransformation processes of antitumour antibiotics, namely the formation of chemically and biologically active free-radical forms of antibiotics, are presented. The ways in which they can be transformed, including the transfer of the electron to oxygen molecules with formation of superoxide radicals, as well as covalent binding to biomacromolecules are discussed. The important role of the acid-base properties of the antibiotics in their free-radical reactions and the characteristics of the biological action of the spin-labelled analogues of anthracycline antibiotics are examined.
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I. INTRODUCTION

The present stage of the development of the experimental chemotherapy of malignant neoplasms, including various aspects of the biochemistry of the cancer cell and the chemical pharmacology of anticancer preparations, is characterised by the wide-scale employment of the ideas and methods of the exact sciences. A combined approach to the solution of the problem of the inter-relation between the structure and biological properties of carcinolytic substances makes it possible to develop the fundamental principles which are essential for the creation of new effective anticancer preparations. An important step in the development of these principles is a new classification of antitumour preparations in terms of the types of their reactivity.[1] This classification is general and, having created the preconditions for a rational planning of the synthesis of anticancer preparations, also permits a more detailed analysis and explanation of the chemical and biological mechanisms of their action. Polyfunctional compounds with hybrid structures and reactivities fit within the framework of this classification. In particular, the majority of antibiotics are preparations of this type.

Antibiotics have been finding in recent years increasingly wide-scale applications in the chemotherapy of malignant diseases. The studies by chemists in this field have been directed towards the synthesis of derivatives of already known antibiotics by their chemical modification and also towards the total synthesis of structural analogues.

The antitumour antibiotics known at present consist of organic compounds of several types from the chemical standpoint, the cytotoxic properties of the majority of which have already been known for a long time. For example, the study of the structure of mitomycin C has demonstrated the presence in its structure of well known cytotoxic groups—benzoquinone, urethane, and aziridine. A whole series of anthracycline antibiotics are characterised by the presence as the aglycone of derivatives of hydroxyanthraquinone, while the carbohydrate fragment consists of aminosugars whose antitumour properties have also been known for a long time. Streptozotocin (a carbohydrate derivative of nitrosomethylurea) was discovered after nitrosocarbamides had been found to possess antitumour properties.

As a consequence of the polyfunctional nature of the antibiotics, studies of the role of various chemical mechanisms

(electrophilic substitution, complex formation, and free-radical reactions) in the manifestation of the biological effect are extremely important.

The oxidation-reduction biotransformation processes involving the majority of antitumour antibiotics, accompanied by the intermediate formation of free radicals, have become the subject of numerous investigations during the last decade. To a large extent, this is associated with the important biological role of the endogenic (including metabolically active) and exogenic free radicals and also with the possibility of their detection in various biological media by electron paramagnetic resonance.

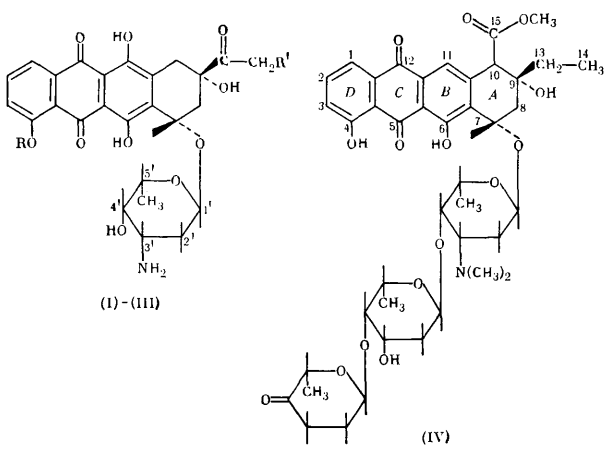
It is noteworthy that ideas concerning the free-radical mechanisms in relation to *in vivo* conditions embrace a wide range of biochemical one-electron transfer processes with participation of paramagnetic species of various types, including free radicals. It is known that, under the influence of many xenobiotics, the content of the radical-ion forms of organic coenzymes and paramagnetic states of metalloprotein molecules increases in organs and tissues and the peroxide oxidation reactions of lipids are activated. Different radical states of xenobiotics, capable of resulting in the formation of active forms of reduced oxygen, are sometimes detected. The action of stable free radicals and other chemical compounds with a paramagnetic centre on living organisms constitues a special case.

Various chemobiological aspects of free-radical mechanisms have also been investigated in connection with the action of antitumour antibiotics. Attention has been concentrated on three types of free-radical species: (1) the radical-ions arising from the antibiotics during their redox reaction; (2) the nitroxy-derivatives of anthracyclines; (3) superoxides. The elucidation of the possible involvement of these radical species in the manifestation of the toxic and antitumour properties of antibiotics is of greatest interest.

II. FREE RADICALS DERIVED FROM ANTITUMOUR ANTIBIOTICS

1. Anthracycline Antibiotics

Antibiotics of the anthracycline series have found wide-scale applications in recent years in the chemotherapy of malignant tumours. The best known representatives of this class of antitumour preparations are adriamycin (I), rubomycin (daunomycin) (II), carminomycin (III), and aclacinomycin A (IV).[2] Despite the large differences in their biological activites, these antiobiotics are close chemical analogues:



(I)-(III)

(IV)

R = CH_3, R' = OH (I); R = CH_3, R' = H (II); R = R' = H (III)

The mechanism of the biological action of antitumour anthracycline antibiotics (AAA) is associated with the suppression of the biosynthesis of nucleic acids and (to a much smaller extent) the biosynthesis of protein. Defects in the structure of chromosomes are then observed in dividing cells (fragmentation of chromosomes and mitotic aberrations, mainly the formation of anaphase bridges). Accordingly, the main morphological changes in the cells are associated with changes in the size and shape of the nucleoli and with the appearance of fine-grain chromatin.[3]

The cytotoxic effect of the AAA depends on their concentration, the duration of their action, and the method by which they are introduced into the organism. Thus it has been shown that their action on tumour cells *in vitro* depends on their extracellular concentration and the time of exposure to these substances[4] and the surviving fraction of tumour cells N is described by the relation

$$N = N_0 e^{-ktc},$$

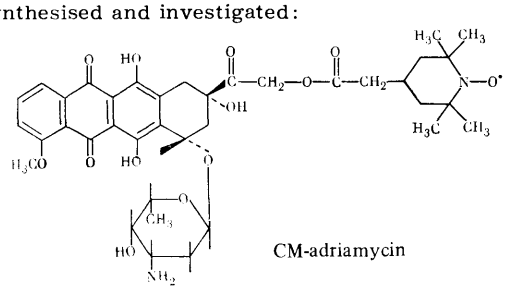
where t is the duration of exposure (min) and c the extracellular concentration of the AAA (μg mol^{-1}). The constant k (mol μg^{-1} min^{-1}) characterises the sensitivity of particular tumour cells to the given preparation. k = 0.045 mol μg^{-1} min^{-1} for the fibroblasts of the Chinese hamster and k = 0.050 mol μg^{-1} min^{-1} for *HeLa* cells. There is a direct correlation between the extracellular and intracellular AAA concentrations. However, there is no proportionality between the duration of exposure and the intracellular concentrations of the preparations.[4]

The differences in the sensitivities to the action of the AAA are also associated with the processes involving their accumulation in the cells. Thus the preparation penetrates readily into L-1210/R leukaemia cells, which are resistant to the action of rubomycin, but it is rapidly metabolised within them; on the other hand, in the L-1210 and P-388 cells, which are sensitive to the preparation, rubomycin persists in the course of 24 h. In chemotherapy the method of introduction and the pharmacokinetic behaviour of the AAA play an important role. The maximum chemotherapeutic effect is attained when the AAA is introduced by methods which ensure direct contact between the preparation and the tumour cells. This fact, which is fairly self-evident from general considerations, has been demonstrated[5] in relation to the B-16 melanoma, which had been grafted intra-abdominally or subcutaneously. A much greater amount of adriamycin penetrates tumour cells and is contained within them for the intra-abdominal growth of the tumour and the intra-abdominal introduction of the preparation.

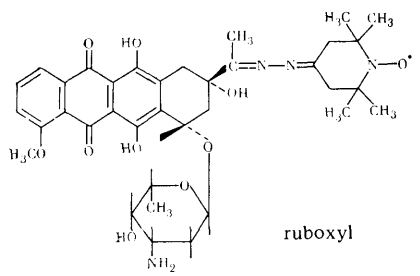
Many AAA derivatives and complexes based on them, differing in their pharmacokinetic behaviour in the organism, have been synthesised in order to increase the efficiency of the chemotherapeutic action. The following complexes have been obtained and investigated: AAA–DNA,[6] AAA–dextran,[7] AAA–aminoacids,[8] AAA-3 × Fe^{3+},[9] AAA incorporated in liposomes,[10] as well as complexes of adriamycin with antibodies,[11] which were distinguished by excellent antitumour properties and a reduced cardiotoxicity.

Among the numerous studies of the chemical modification of the AAA, it is possible to isolate researches[12–14] into the synthesis of nitroxy-derivatives of the AAA which have priority. Such modification of the structure of anthracyclines imparts to them the properties of organic paramagnetic materials where the presence of the free-radical centre alters significantly the oxidation-reduction properties of the preparations and their capacity for involvement in reactions with transfer of one electron. Spin-labelled derivatives of adriamycin (the nitroxy-fragment is linked to the aglycone by an ester bond) and rubomycin (the nitroxy-

fragment is linked to the aglycone via an azine bridge) have been synthesised and investigated:



CM-adriamycin



ruboxyl

The introduction into the antibiotic molecule of fragments containing a free-radical centre entails an appreciable decrease of acute toxicity and an increase of the antitumour activity of the preparations (Table 1). The characteristics of the reduction of nitroxy-fragments and the pharmacokinetic features of the modified AAA have been studied by EPR. The possible chemical causes of the differences in the pharmacokinetic behaviour of nitroxy-derivatives of the AAA can be associated with the differences in the rates and mode of enzymic reduction. Among several possible reduction centres (quinonoid, ketone, and nitroxy-groups), the free-radical fragment undergoes preferential reduction.

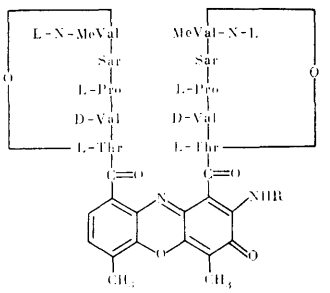
Table 1. Comparative data for the acute toxicities and antileukaemic activities of ruboxyl and rubomycin.[14]

Preparation	LD_{50}, mg kg^{-1}	ILS, %	
		P-388 leukaemia	La leukaemia
Ruboxyl	44.0	155	243
Rubomycin	5.6	68	63

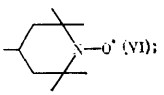
Notation: LD_{50} is a single dose of the preparation inducing the death of 50% of the experimental animals (mice) and ILS is the increase of the average lifespan compared with the control.

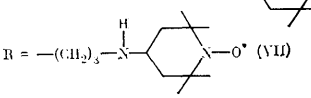
The interaction of a spin-labelled analogue of adriamycin (CM-adriamycin) with DNA has been studied by EPR.[13] In the first place one should note the resistance of the ester linkage in CM-adriamycin to hydrolysis when it interacts with DNA. At neutral pH the EPR spectra of the complex of CM-adriamycin with DNA remain unchanged in the course of several days, which indicates the absence of the hydrolytic scission of the nitroxy-fragment. The form of the EPR spectra of CM-adriamycin does not depend on its relative concentration under conditions where there are between one and four antibiotic molecules for 20 pairs of DNA bases. The subsequent increase of the CM-adriamycin concentration results in the appearance in the high-field region of the EPR spectrum of a narrow line characteristic of CM-adriamycin in solution (Fig.1). Analysis of the EPR spectra established that under these conditions CM-adriamycin forms a complex with DNA as a result of intercalation between the nitrogen-containing bases.[13]

An analogous mechanism of the interaction with DNA is characteristic also of certain other polycyclic compounds, for example, the antibiotics of the actinomycin series. The spin-labelled analogues of actinomycin D have been studied:[15]



(V)-(VII)

R = H (V), actinomycin D; R =  (VI);

R =  (VII)

It is of interest that the nitroxy-derivatives of actinomycin D were bound to DNA to a lesser extent than the initial antibiotic and caused a lower degree of inhibition of the DNA-dependent RNA-polymerase. On the other hand, in experiments on P-388 leukaemia the spin-labelled analogue of actinomycin D showed an antitumour effect which was better by a factor of 1.5.[15] This example indicates the absence of a relation between the degree of intercalation and the antitumour activity of antibiotic derivatives containing a free-radical fragment.

A comparative study of adriamycin, carminomycin, and the 11-methyl ether of carminomycin on the Novikov ascites hepatoma *in vitro* showed that their cytotoxic effects could not be accounted for by their capacity to inhibit the biosynthesis of nucleic acids or to bind on to DNA molecules.[16] Nevertheless the different types of the biological action of anthracyclines (cytotoxic mutagenic, and carcinogenic effects) are explained mainly by the capacity of AAA for intercalation between the DNA bases.

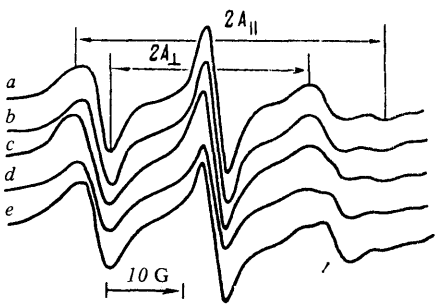
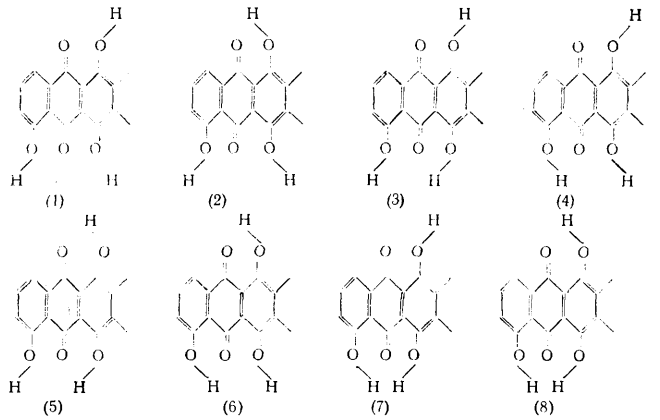


Figure 1. Variation of the EPR spectra of spin-labelled adriamycin in the presence of DNA with its concentration (0.01 M NaCl and 1.2 mg ml^{-1} DNA). Ratio of the antibiotic and DNA (base pairs): *a*) 1:20; *b*) 2:20; *c*) 4:20; *d*) 7:20; *e*) 10:20.[13]

An alternative point of view on the molecular mechanisms of the biological action of AAA, involving the formation of free-radical intermediates, attracts attention in this connection. The characteristics of the chemotherapeutic properties of anthracyclines can be accounted for by the different capacities for donor–acceptor interactions, different permeabilities, and different oxidation-reduction properties of the preparations. The attempts at a rigorous quantitative description of the individual properties of AAA and to establish correlations between the structure and the biological activity of the test substances have now acquired fundamental importance.

Quantum-chemical calculations for the model analogues of the AAA aglycones and the corresponding radical-anions for isolated molecules and their hydrate complexes have demonstrated the necessity to take into account the influence of the solvent on their electronic and conformational properties, since solvation effects can lead to significant conformational rearrangements. The semi-empirical INDO and CNDO/2 methods provide a fairly satisfactory qualitative description of the state of the system, although they yield less realistic solvation energies and hydrogen bond strengths than *ab initio* methods. Calculations of the structures of hydrate complexes incorporating four water molecules have been carried out taking into account the formation of hydrogen bonds involving the oxygen atoms of the anthraquinone fragment.[17]



It has been found that, in terms of the isolated molecule approximation, the formation of intramolecular hydrogen bonds is favoured by energy factors and the appearance of each succeeding bond causes a proportional reduction in the total energy of the system. It has been demonstrated in relation to hydrate complexes that the formation of intermolecular hydrogen bonds is easier than that of the intramolecular hydrogen bonds of hydroxyanthraquinone (Table 2).[17]

Table 2. Calculated formation energies of the intramolecular hydrogen bonds ($\Delta E_b = E_i - E_1$) in isolated molecules and the solvation energies of the tetrahydrate complexes of carminomycin for different conformations of the hydroxy-groups of the anthraquinone ring (ΔE_h).[17]

Structure	ΔE_b, kcal mole^{-1}	ΔE_h, kcal mol^{-1}	Structure	ΔE_b, kcal mole^{-1}	ΔE_h, kcal mol^{-1}
(1)	0	59.8	(5)	15.5	36.2
(2)	7.6	47.2	(6)	17.1	33.2
(3)	8.1	49.0	(7)	17.3	42.5
(4)	9.5	46.4	(8)	24.9	28.2

The distribution of charges and spin densities in the corresponding radical-anions has been investigated taking into account the structure of the isolated neutral molecules and the hydration effects of aglycones. The formation of radical-anions entails the rearrangement of the atomic structure in the chromophoric part of the AAA. The main electronic charge is localised under these conditions at the oxygen atoms of the carbonyl groups: $\Delta q_5 = q_5^a - q_5^n = 8.25 \times 10^{-2}$e and $\Delta q_{12} = 7.41 \times 10^{-2}$e. The unpaired electron is in the lowest unoccupied π_z orbital of the anthraquinone ring, while the spin densities have the maximum value at the oxygen atoms of the carbonyl groups ($\rho^5_{\pi z} = 0.489$; $\rho^{12}_{\pi z} = 0.443$) and at the carbon atoms of the carbonyl groups ($\rho^5_{\pi z} = 0.107$; $\rho^{12}_{\pi z} = 0.128$).

The theoretical spin densities at the hydrogen atoms of the carminomycin aglycone (with and without allowance for hydration) are presented in Table 3. Analysis of these data shows that the experimental splittings in the EPR spectrum ($a_H = 4.1$ G and $a_H = 2.1$ G) can be explained by the interaction of the unpaired electron with the protons of the *A* ring. The HFS constants can be determined from the formula $a(G) = K\rho^S$, where ρ^S is the spin density in the *s* orbital of the proton and *K* a constant equal to 539.86 for hydrogen atoms.[18] The theoretical spin density distributions for the aglycones of other AAA differ little from the data for carminomycin. The splittings by the protons of the *A* ring differ somewhat for the two possible conformations, namely chair and half-chair, but a choice in favour of the existence of a particular conformation in solution cannot be made on the basis of the calculated values.

Table 3. The spin densities in the *s* orbitals of the hydrogen atoms ($10^2\rho^S$) in the radical-anions of carminomycin aglycones calculated for the conformation of the hydroxy-group corresponding to structure (1) for different conformations of the *A* ring [*a*) without allowance for the hydration of anthraquinone; *b*) with allowance for the hydration of anthraquinone[17]].

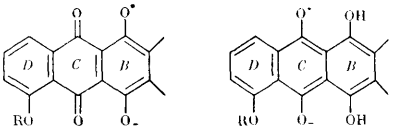
H atom	Chair		Half-chair	
	a	*b*	*a*	*b*
H(1)	0.01	−0.03	0.02	−0.03
H(2)	−0.01	−0.01	−0.02	−0.02
H(3)	−0.10	−0.11	−0.10	−0.11
H(4)	0.01	0.01	0.00	0.01
H(6)	0.01	0.01	0.00	0.00
$H(7)^{OH}$	0.53	0.50	0.47	0.38
H(7)	−0.09	−0.09	−0.46	−0.44
H(8)	−0.03	−0.03	−0.02	−0.02
H(8)	−0.05	−0.04	−0.01	−0.01
H(10)	0.46	0.41	0.52	0.27
$H(10)^a$	0.91	0.80	0.74	0.77

Notation: $H(7)^{OH}$ is the hydrogen atom of the hydroxy-group in the 7-position in the aglycone and $H(10)^a$ is the axial hydrogen atom in the 10-position.

An important result of the calculations is the conclusion that the C(7)–O(7) bond is weakened on formation of the radical-anions, which follows from the analysis of Wiberg's indices. Such weakening of the bond, deduced from theoretical calculations for model compounds, shows that the reduction of the AAA can entail the scission of a hydrocarbon fragment (Table 4).[17] Indeed this has been confirmed experimentally. For example, it has been shown[19] that, in the enzymic reduction of rubomycin under the conditions of hypoxia, the consumption of the antibiotic is

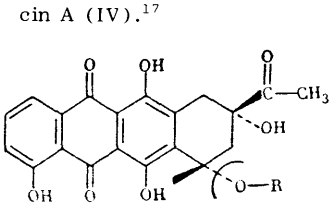
accompanied by an increase of the content of the free aglycone in the system (Fig.2). Anthracycline antibiotics are gradually converted in the cell into deoxyaglycones, which are more lipophilic and possibly more strongly bound to the membranes of microsomes. According to a quantum-chemical calculation, the reduction of aclacinomycin A can be accompanied by the elimination of the 15-methoxy-group as well as the hydrocarbon fragment (Table 6).

These results indicate the potentially important role of the oxidation-reduction reactions with the intermediate formation of free-radical states. One might have expected the formation of free radicals from AAA both as a result of the oxidation of the hydroquinone group (the *B* ring) and as a result of the reduction of anthraquinone (the *C* ring).

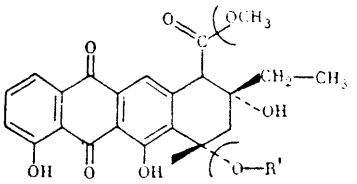


The free-radical intermediates formed under these conditions are characterised by different reactivities, which may be the reason for the selectivity of the biological action of AAA, in particular it may determine the ratio of the degree of toxicity to the antitumour effect.

Table 4. The Wiberg bond orders in the neutral molecules and radical-anions of carminomycin (III) and aclacinomycin A (IV).[17]



(III)



(IV)

State	(III)		(IV)				
	C(7)–O(7)	O(7)–R	C(7)–O(7)	O(7)–R′	C(10)–C(15)	C(15)=O	C(15)–O
Neutral molecule	0.4620	0.4890	0.4790	0.4790	0.4866	0.9274	0.4849
Radical-anion	0.4522	0.4950	0.4631	0.4793	0.4891	0.9319	0.4740

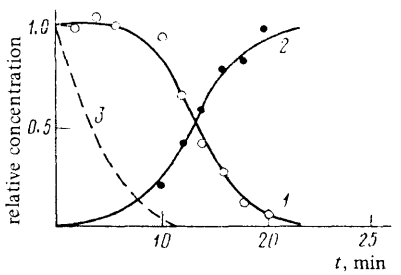


Figure 2. Kinetic curves for the variation of the contents of rubomycin (curve *1*) and its aglycone (curve *2*) and of the partial pressure of oxygen (curve *3*) in the microsomal system in the presence of NADPH (according to the data of Bachur et al.[29]

The capacity of the AAA aglycones for reduction and oxidation has been estimated on the basis of the calculation of the energies of the lowest unoccupied molecular orbital (E_{LUMO}) and the highest occupied molecular orbital (E_{HOMO}).[20] The values of E_{LUMO} and E_{HOMO} for carminomycin, rubomycin, adriamycin, and aclacinomycin A and their O_6^- anions are presented in Table 5. Evidently in the neutral state all the aglycones have similar values of both E_{LUMO} and E_{HOMO}. Consequently the anthracycline antibiotics examined above have approximately the same electron-accepting properties. The extremely high absolute values of E_{HOMO} show that in the neutral state all the aglycones are fairly resistant to oxidation. On the other hand, the AAA anions, characterised by much lower values of E_{HOMO}, exhibit an increased capacity for oxidation. It follows from Table 7 that the aclacinomycin A anion showed the lowest capacity for oxidation, which was in fact to be expected in view of the absence of the hydroquinone fragment from its structure. The most pronounced electron-donating properties are characteristic of the carminomycin aglycone anion.

Table 5. The energies of the HOMO and the LUMO for the neutral molecules and anions in the series of anthracycline antibiotics and their toxicity on intra-abdominal administration.[20,21]

Parameter	Carminomycin	Rubomycin	Adriamycin	Aclacinomycin A
E^n_{HOMO}, eV	−10.306	−10.288	−10.217	−10.342
E^a_{HOMO}, eV	−3.203	−3.209	−3.288	−3.670
E^n_{LUMO}, eV	0.690	0.690	0.719	0.633
E^a_{LUMO}, eV	4.680	4.678	4.810	3.695
LD_{50}, mg kg^{-1}	1.3	5.5	8.5	25.0
pK_a	8.4	9.6	9.6	9.0

Notation: E^n_{HOMO} and E^n_{LUMO} are the energies of the HOMO and the LUMO of the neutral molecules of the AAA aglycones and E^a_{HOMO} and E^a_{LUMO} are the energies of the HOMO and LUMO of the anions of the AAA aglycones.

Table 6. Covalent binding of [^{14}C]adriamycin labelled in the 14-position to microsomal proteins.[13]

Experimental conditions	α, %
Denatured microsomes + adriamycin + NADPH	1.1
Microsomes + adriamycin	0.8
Microsomes + adriamycin + NADPH	4.4
Microsomes + adriamycin + SOD	1.0
Microsomes + adriamycin + NADPH + SOD	4.5

Notation: SOD is superoxide dismutase and α is the fraction of the bound radioactive label.

The oxidation-reduction properties of the AAA at physiological pH can be influenced by the acid–base characteristics of the aglycones. The study of the electronic absorption spectra of the antibiotics in the visible region at different pH of the medium demonstrated the presence of isosbestic points (Fig.3), which indicates the existence of equilibrium

in alkaline solutions between the neutral and ionised forms of the antibiotics. It follows from the data presented in Table 5 that at physiological pH the molecules of the anthracycline antibiotics are in a partly ionised state.

The formation of the ionised form of the AAA is a fairly complex process owing to their polyfunctional character. Apart from the aglycone hydroxy-groups, capable of dissociation, the nucleophilic centres of the molecules, responsible for the possibility of association, also participate in the process. For example, the formation of dimers in aqueous rubomycin solutions (5×10^{-8} M) has been demonstrated spectrophotometrically and by the NMR and circular dichroism methods.[22] At a constant pH a decrease of the degree of dissociation is therefore observed with increase of the AAA concentration.

Table 7. The rate (w) of the microsomal oxidation of NADPH stimulated by various antitumour preparations.[26]

Preparation	w, nmol/mg protein per min	
	air	CO
Control	0	0
Adriamycin	73	84
Mitomycin C	84	81
Bruneomycin	249	209
Lapachol	15	11
Cyclophosphane	0	0
Methotrexate	0	0
N,N'-Di(chloroethyl)-N-nitrosourea	0	0

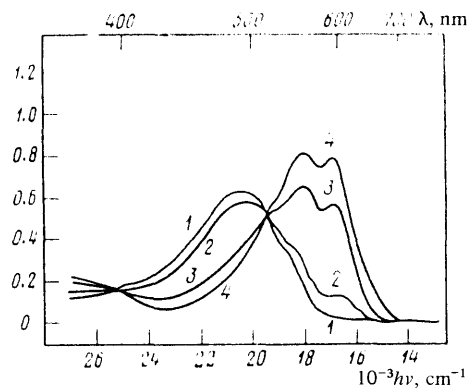


Figure 3. Optical absorption spectra of rubomycin at different pH of the medium: 1) 6.8; 2) 9.2; 3) 10.5; 4) 13.[20]

For a comparative study of the electron-donating properties of the AAA, the reaction involving the oxidation by potassium hexacyanoferrate(III) has been investigated.[20] The dependence of the effective rate constants k_{eff} for their oxidation reaction on the oxidant concentration and the pH of the medium was studied. Fig.4 illustrates the variation of k_{eff} with the oxidation of carminomycin, rubomycin, and adriamycin as a function of the hexacyanoferrate(III) concentration at pH 7.6. Evidently the replacement of the hydrogen atom in the 14-position by the hydroxy-group does not influence the electron-donating properties of the antibiotics. On the other hand, the replacement of the 4-methoxy-fragment by the hydroxy-group decreases sharply the pK_a of the aglycone and enhances its electron-donating properties. The oxidation rate constant depends markedly on the pH of the medium. Thus, in the oxidation of rubomycin and carminomycin (5×10^{-5} M) with potassium hexacyanoferrate (III) (5×10^{-3} M), it was found that k_{eff} is 0.3×10^{-2} s^{-1} and 0.7×10^{-2} s^{-1} respectively at pH 7.0, while 1.3×10^{-2} s^{-1} at pH 8.0 was obtained. The oxidation of the relatively non-toxic aclacinomycin A by the hexacyanoferrate(III) was not observed even at pH 9.5.

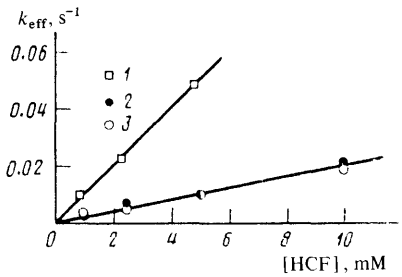


Figure 4. Dependence of the rate constants for the oxidation of different antibiotics on the concentration of hexacyanoferrate(III) (HCF) (pH 7.6, T = 25 °C):[20] 1) carminomycin; 2) rubomycin; 3) adriamycin.

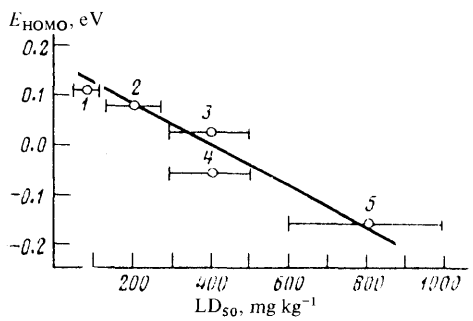


Figure 5. Correlation between the energies of the highest occupied molecular orbitals of the reduced forms (R^-) of derivatives of 2,2,6,6-tetramethyl-4-X-piperidine N-oxides [X: 1) $-(CH_2)_2NH_2$); 2) $-OC(O)NHPh$; 3) $-OH$; 4) $-NHC(O)-NCH_2CH_2$; 5) $=O$] and acute toxicity (LD_{50}).[24]

Thus the electron-donating properties of the AAA are enhanced in the sequence aclacinomycin A < adriamycin ≅ rubomycin < carminomycin; their acute toxicity increases at the same time (LD_{50}) diminishes. When account is taken of these results, the diminution of the cytotoxic properties of the 11-methyl ether of carminomycin can be accounted for by the modification of the structure accompanied by a decrease of the capacity for oxidation (there is no hydroquinone fragment in the structure).

A statistically reliable correlation between the LD_{50} for a series of 4-substituted derivatives of the 2,2,6,6-tetramethylpiperidin-1-yloxy-radical and the E_{HOMO} of the corresponding anions is noteworthy in this connection (Fig.5).[24] The linear regression equation has the following form with a reliability of 95%:

$$LD_{50} = aE_{HOMO} + b,$$

where $a = -2352 \pm 1208$ and $b = 371 \pm 119$. This result shows that the processes involving the oxidation of the reduced forms of the nitroxy-radicals are responsible for their toxicity and not reactions involving the endogenic reduction.

The above correlation between the capacity for oxidation and the toxic properties of antitumour preparations must be taken into account in their chemical modification and in the development of combined polychemotherapy. However, at the present time the formation of free radicals from anthracycline antibiotics has been studied mainly under the conditions of their reduction.

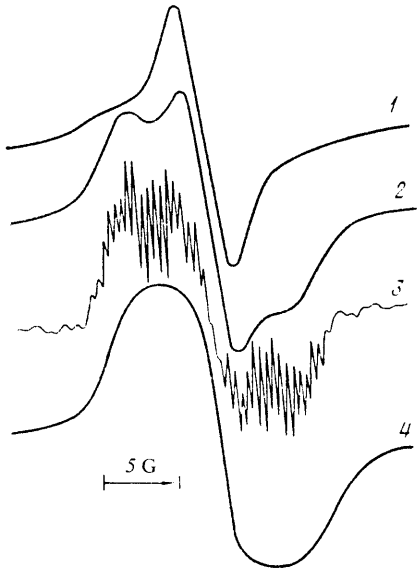


Figure 6. Changes in the EPR spectrum of the rubomycin semiquinone radicals obtained on reduction with KBH_4 after different periods (min): 1) 2; 2) 5; 3) 6; 4) 30.[17]

On reduction of rubomycin in water with potassium tetrahydroborate, an intense signal ($g = 2.004$ and $\Delta H = 4$ G) due to the primary semiquinone radical appears in the EPR spectrum during the first two minutes. After only three minutes, another signal ($g = 2.004$, $\Delta H = 12$ G) with a characteristic hyperfine structure appears against the background of the first. After a further few minutes, both signals become broadened and are recorded as one singlet with a width of 9 G (Fig.6). At the same time a precipitate is formed in the reaction mixture, which may be associated with the elimination of the carbohydrate fragment and the formation of the radical forms of the aglycones, which are sparingly soluble in water. On reduction of the AAA in methanol, stable radicals with a well resolved hyperfine structure are detected.[17]

The spontaneous formation of semiquinone AAA radicals has also been observed at physiological pH values. In this case the rate of formation of the radicals is independent of the oxygen content, but the semiquinone radicals produced are destroyed by oxygen atoms. The rate of formation of the adriamycin semiquinone radicals (20 mg ml^{-1}) varied from 7.0 nmol min^{-1} at pH 7.65 to 48.0 nmol min^{-1} at pH 8.85.[25]

The formation of free radicals has also been demonstrated on enzymic reduction of AAA.[26-30] Semiquinone radicals are detected by EPR when AAA are incubated with cells of the Ehrlich ascites carcinoma[26,27] and also with the microsomal or nuclear fraction of rat liver cells under the conditions of hypoxia in the presence of NADPH.[25,28-30] Electron transfer from the AAA to NADPH is catalysed by one-electron transfer flavoproteins such as NADPH-cytochrome P-450 reductase, nitrate reductase, and NADPH-cytochrome *c* reductase, which indicates the absence of specificity in the reduction of the quinonoid group in the AAA. Reductases of various types are capable of reducing the oxo-group of rubomycin in the 13-position with formation of 13-dihydrorubomycin (daunomycinol). Adriamycin and carminomycin undergo analogous reactions, but are transformed much more slowly. The reduction of the oxo-group can be catalysed by the aldoketoreductase from rat kidneys and liver in the presence of NADPH.[31] On treatment with reductases, the sugar fragment can be split off with formation of free aglycones, but the reduced aglycones are 100 times less active than the initial AAA.[5] This is apparently associated with the lower solubility of the AAA aglycones and the consequent pharmacokinetic characteristics.

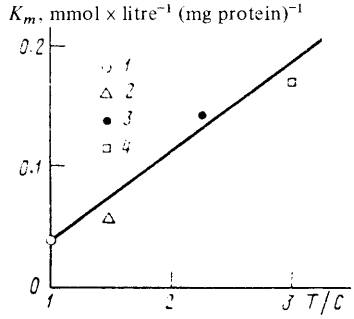


Figure 7. Relation between the antitumour effectiveness (T/C) and the Michaelis constants K_m in the enzymic reduction of rubomycin: 1) L-1210/R; 2) L-1210; 3) P-388; 4) B-16 (T is the lifespan of the animals in the experimental group following the administration of the rubomycin and C the lifespan of control animals) (according to the data of Yesaik et al[5]).

The sensitivity of tumour cells to the AAA depends on the presence in the former of enzyme systems capable of activating and metabolising the AAA. Thus rubomycin is reduced to daunomycinol most vigorously in the cells of the B-16 melanoma—the tumour which is most sensitive to the action of the AAA. This indicates the importance of the enzyme activity of rubomycin in tumours and the possible role of daunomycinol in the manifestation of the antitumour effect (Fig.7). In this connection one can also note that the local

hyperthermia of the tumours increases the effectiveness of adriamycin against the background of the increased intensity of its metabolism.[32]

Two-electron transfer enzymes such as glutathione reductase and lactate dehydrogenase are not involved in the formation of radicals.[30] The kinetics of the reduction of quinones by flavoproteins depend both on the redox potentials of the quinones and on the enzymes catalysing their reduction. Thus the lower limit of the redox potential for the reduction of quinones by the NADPH-cytochrome P-450 reductase is -240 mV, while for NADPH-cytochrome P_5 reductase and NADH-ubiquinone oxidoreductase the limit is -170 mV. Lipophilic properties apparently play a small role in the reduction of these preparations by enzymes.[33]

The EPR spectrum of the semiquinone metabolites of anthracyclines in microsomes does not appear immediately, arising after the consumption of the oxygen dissolved in them and is then observed over a period of several hours.[27] During the incubation of the antibiotics with microsomes, the partial pressure of oxygen diminishes owing to electron transfer from the semiquinone species to oxygen.[26,29,30,34,35] So long as oxygen is present in the microsomes, the signal of the semiquinone radicals is not observed in the EPR spectrum of the antibiotic. As the partial pressure of oxygen diminishes, the EPR signal referring to the semiquinone radical of the anthracycline begins to be detected. The initially symmetrical signal with $g = 2.0036$ then becomes asymmetric and after several hours the spectrum assumes the character of a strongly delayed axially symmetrical signal with $g = 2.0046$ and $g = 2.0021$.[27]

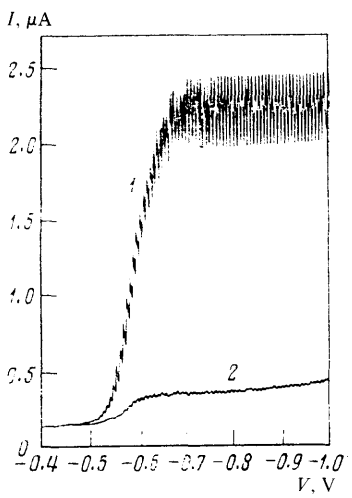


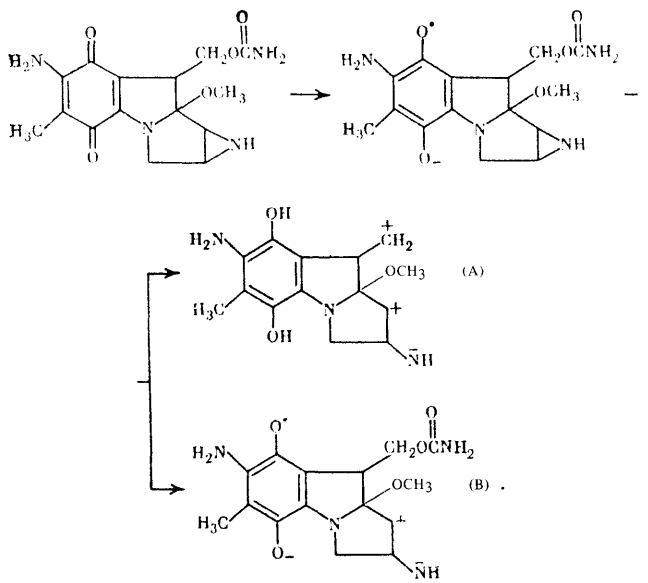
Figure 8. Polarographic reduction wave: 1) rubomycin; 2) rubomycin + DNA (molar ratio DNA : rubomycin = 8.7 : 1).[3]

The anthracycline antibiotics intercalated between the DNA bases are poorly reduced to semiquinone radicals, which agrees with the absence of a polarographic reduction wave of rubomycin after the latter has been incubated with DNA[3] (Fig.8). Antitumour anthracycline antibiotics linked to DNA are poorly reduced by microsomes following the addition of NADPH, so that only a weak signal due to semiquinone radicals is then detected by EPR.[27] All this shows that the AAA intercalated in DNA are "poor" substrates for enzymic reduction.

On chemical and biological activation, AAA molecules are capable of binding covalently to biomacromolecules, which is due to the intermediate formation of semiquinone radicals.[36] The degree of covalent binding of rubomycin to DNA under ultraviolet irradiation increases by a factor of 3 in the presence of oxygen.[36] Covalent binding of adriamycin to microsomal proteins takes place only in the presence of NADPH, which ensures the enzymic reduction of the preparation to a semiquinone. The addition of superoxide dismutase did not affect the binding of adriamycin to microsomal proteins, which rules out the involvement of the superoxide radicals in the process (Table 6).[37]

The generation of semiquinone radicals investigated in relation to anthracyclines can probably be important also for other antibiotics containing quinonoid (or analogous) fragments in their structure. Preparations, in the mechanism of the biological action of which processes involving the intermediate formation of free radicals, can play an important role, are considered below.

Mitomycin C. In 1956 an involved set of substances with antibiotic properties which effectively inhibited the growth of the Ehrlich ascites tumour were isolated from the culture medium of *Streptomyces caspitosus*. Later an individual compound, called mitomycin C, was isolated from this mixture. A rapidly acting bactericidal and cytotoxic antibiotic, mitomycin C is used in the treatment of the cancer of the stomach, the mammary gland, and the pancreas.[38] The possible pathways leading to the chemical activation of mitomycin C, including the formation of carbonium ions and semiquinone radicals, indicate a polyfunctional character of this antibiotic:



The cytotoxic activity of mitomycin C can be accounted for by its capacity both to alkylate monofunctionally the DNA bases (probably as a result of the opening of the aziridine ring) and its capacity to form cross-links between the complementary DNA chains[39-41] in consequence of the bifunctional nature of the mitomycin C intermediates. It has been shown that the DNA incubated with the antibiotic for 1 min

is characterised by the presence of covalent bonds (cross-links) between the complementary chains, which can be readily observed on the basis of the reversibility of its denaturation process.

One of the possible mechanisms of this process involves the formation of intermediates of type (A) with two electrophilic centres arising from the urethane and aziridine groups of mitomycin C. Another pathway involves the formation of the free-radical intermediate (B), which can take place in several stages. The most probable (by a factor of 10–20) monoalkylation process occurs initially and is followed by the generation of semiquinone radicals. This is indicated by the finding that the mitomycin C bound covalently to DNA is also capable of being reduced to a semiquinone radical, whose interaction with oxygen leads to the formation of superoxide radicals.[39] On chemical or enzymic reduction, mitomycin C is converted into a highly reactive bifunctional agent forming covalent bonds with nucleic acids, proteins, and other molecules in the damaged cells. The bifunctionality can therefore be a consequence of the formation from the preparation of semiquinone radicals containing an electrophilic centre consisting of the opened aziridine ring (B). The reduced mitomycin also exhibits a high reactivity and is readily bound to DNA *in vitro*, forming cross-links in the latter. The active form (B) of mitomycin C is apparently extremely unstable since the cross-links arise in DNA only if DNA is added a few seconds after the reduction of the antibiotic. Reduced mitomycin is bound initially to the guanine residues in DNA but can also readily interact with RNA and cell proteins.

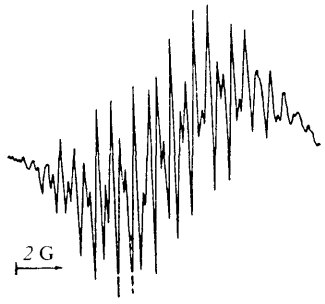
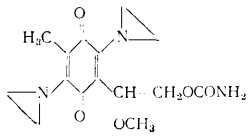


Figure 9. EPR spectrum of the semiquinone radical of mitomycin C reduced with $NaBH_4$ in phosphate buffer at pH 7.0.[39]

The reduction of a solution of mitomycin C in dimethyl sulphoxide (DMSO) by sodium tetrahydroborate leads to the formation of a stable semiquinone radical, whose EPR spectrum contains 36 lines with the splittings $a_{NH_2} = 2.3$ G, $a^N_{ring} = 1.7$ G, $a^H_{CH_3} = 1.0$ G, and $a^H_{CH_2} = 0.65$ G with $g = 2.0046$ (Fig.9).[39] The observation and detection of the semiquinone radicals of mitomycin C in an aqueous medium is complicated by their comparatively short life. When the preparation was incubated with microsomes in the absence of oxygen, the EPR signal of the semiquinone radical of mitomycin C with $g = 2.0035$ and $\Delta H = 9$ g, vanishing in the course of 4 min, was recorded. The signal appears only in the joint presence of mitomycin C, microsomes, and the NADPH-generating system (0.39×10^{-3} M NADH, 5.5×10^{-3} M glucose-6-phosphate, and 0.67 unit ml^{-1} of glucose-6-phosphate dehydrogenase). In terms of its spectroscopic characteristics ($g = 2.0034$), it is identical with the signal recorded on chemical reduction of mitomycin C in an aqueous medium.[27]

It must be emphasised that mitomycin C bound covalently to poly G, poly C also gave rise to a spectrum characteristic of the semiquinone radical following its reduction with $NaBH_4$.[39]

Carboquone, used in the treatment of leukaemia, is a close structural analogue of mitomycin C.



Carboquone has two polarographic reduction waves at −0.23 and −1.6 V relative to the saturated calomel electrode. In liver microsomes in the presence of NADPH carboquone is reduced to a semiquinone radical; its EPR spectrum is characterised by well-resolved hyperfine structures (Fig.10), which can be accounted for by the interaction of the unpaired electron with the three equivalent protons of the methyl group in the 6-position ($a^H_{CH_3} = 0.55$ G) and with the two nuclei of the nitrogen in the aziridine groups in the 2- and 5-positions ($a^N_{N(2)} = 2.78$ G; $a^N_{N(5)} = 3.03$ G). After the incubation of carboquone with Ehrlich ascites tumour cells, the formation of carboquone radicals is also detected. The addition of DNA or glucose under these conditions does not influence the radical formation process.[28]

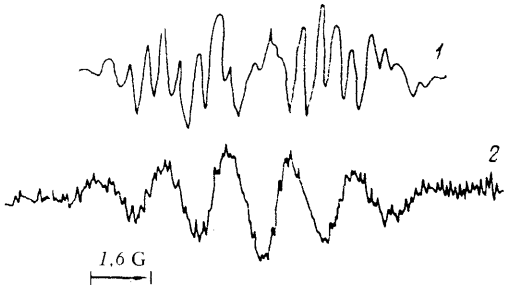
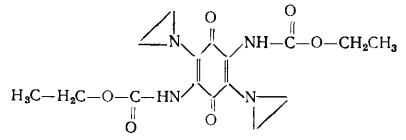


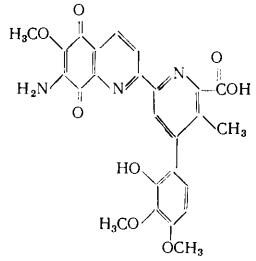
Figure 10. EPR spectra for the semiquinone radicals of carboquone (curve *1*)[28] and AZQ (curve *2*)[42] obtained on microsomal reduction in the presence of NADPH.

Another structural analogue of mitomycin C is the quinone-containing alkylating agent AZQ, which can also be reduced in microsomes to semiquinone radicals:[42]



Bruneomycin. Bruneomycin has been obtained in the USSR from a culture of *Streptomyces albus var bruneomicini* and is identical with the foreign compounds streptonigrin

and rubochromomycin. It is used in the treatment of lymphogranulomatosis, chronic lympholeukaemia, reticulosis and certain other systemic diseases of the blood as well as the kidney adenosarcoma (Wilm's tumour) and neuroblastoma, which are resistant to other antitumour preparations.[43] Bruneomycin suppresses the synthesis of DNA in animal and bacterial cell cultures. It remains bound to DNA isolated from ascites tumour cells of mice.



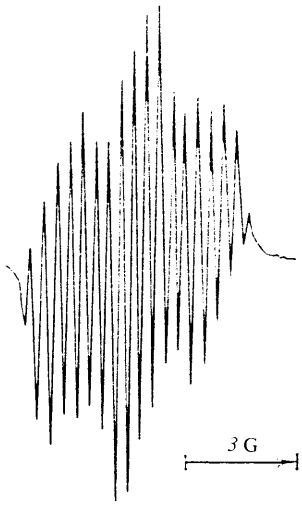
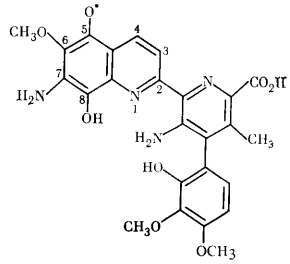


Figure 11. EPR spectrum of the bruneomycin radical (4×10^{-4} M) obtained on reduction with $NaBH_4$ (8×10^{-4} M) in phosphate buffer at pH 7.0.[39]

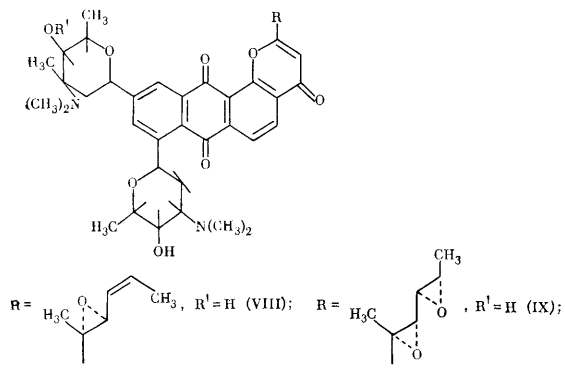
As in the case of mitomycin C, the batericidal action of bruneomycin is accompanied by the degradation of DNA molecules but it does not induce the formation of DNA cross-links.[3] The simultaneous presence of a source of electrons and oxygen is essential for the manifestation of the maximum bactericidal activity.[43] The reduction of bruneomycin by KBH_4 in DMSO in the absence of oxygen led to the formation of a semiquinone radical whose spectrum is characterised by the constants for splitting by the nitrogen atoms in 7- and 1-positions ($a^N_{N(7)} = 0.9$ G and $a^N_{N(1)} = 0.3$ G) and also by the proton in the 4-position (2.1 G) and by the two-equivalent protons of the amino-group (0.3 G).[39]

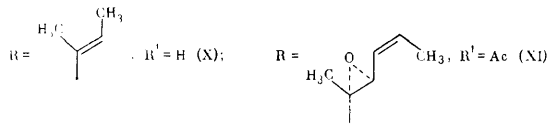


An analogous EPR spectrum has been recorded also on biological reduction of bruneomycin in a suspension of *E.coli* cells, which suggests an important role of free-radical intermediate states in the molecular mechanisms for the biological action of bruneomycin[44] (Fig.11).

The binding of bruneomycin to nucleic acids in the presence of reducing agents and metal ions has been investigated.[45] Incubation of chemically reduced bruneomycin with DNA *in vitro* was accompanied by irreversible binding and led to the formation of a complex containing one mole of bruneomycin for 250 nucleotides. The presence of Zn^{2+} ions greatly increased the degree of binding and the resulting complex contained one molecule of bruneomycin for 80 nucleotides. On the other hand, the presence of Mg^{2+} diminished such binding. A greater amount of the antibiotic was bound to the denatured DNA than to the native DNA. The maximum degree of binding is attained when bruneomycin is reduced in the presence of DNA. A much greater amount of bruneomycin is bound to DNA following its enzymic activation. Studies with synthetic polynucleotides confirmed that in the presence of Zn^{2+}, bruneomycin is capable of binding to both purine and pyrimidine bases.[45]

Rubiflavin and its analogues. The antitumour bactericidal antibiotic rubiflavin (VIII) has been obtained from *Streptomyces* (SC 3728). Rubiflavin analogues such as hedamycin (IX), kidamycin (X), and pluramycin (XI) also possess antitumour properties.[46] Rubiflavin and hedamycin selectively suppress the synthesis of DNA in the cells and affect the synthesis of RNA to a lesser extent. These antibiotics bind strongly (in actual fact irreversibly) to DNA. Both rubiflavin and hedamycin can be reduced by cultures of *E.coli* with formation of free radicals,[44,47] which indicates the importance of the free-radical states of these antibiotics in the manifestation of their biological activity. Fig.12 presents the EPR spectra of the rubiflavin radical-anions obtained on reduction of the preparation in the cells of *E.coli* and on treatment with KBH_4.[44]





Saframycins A and C. The quinone-containing antitumour antibiotics saframycins A and C have been isolated from *Streptomyces lavendulae*[48] (R = H and R′ = CN for saframycin A and R = OCH_3 and R′ = H for saframycin C):

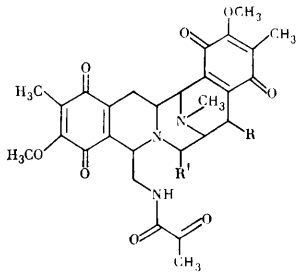




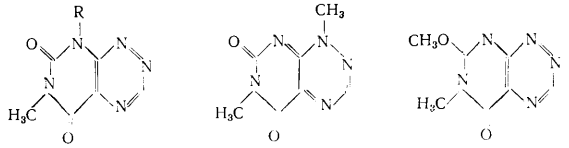
Figure 12. EPR spectra of the rubiflavin radical obtained under different conditions: *a*) on chemical reduction with KBH_4;[44] *b*) on biological reduction in a cell suspension.

Saframycins A and C fully inhibit the growth of L-1210 cells in culture at concentrations of 0.02 and 1.0 μg ml^{-1} respectively. For mice of the C3H/He strain, the LD_{50} of saframycins A and C are 10.5 and 9.7 mg kg^{-1} respectively. The antitumour activity of saframycin A is 50–100 times greater than that of saframycin C. Saframycin A proved to be highly active against P-388 leukaemia and the Ehrlich ascites carcinoma and moderately active against L-1210 leukaemia and B-16 melanoma.[48]

In addition many other natural physiologically active substances contain quinone structures whose action can be associated with the formation of free-radical intermediates. Herbimycin B (XII),[49] javanicin (XIII),[50] the antibiotic WS-5995 A obtained from *Streptomyces auranticolor* (XIV),[51] alkannin (XV),[52] luteoskyrin (XVI),[53] and lapachol (XVII)[54] can be included among preparations of this type.

2. Antibiotics of the Pyrimido [5,6-*e*] -1,2,4-triazine Group

Antibiotics of this series include reumycin, fervenulin, xanthothricin, and 7-methoxyreumycin.



R = H, reumycin
R = CH_3, fervenulin

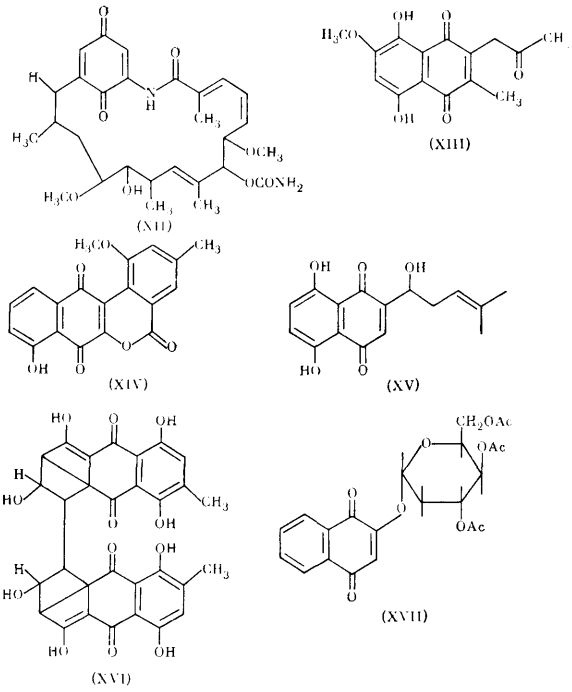
xanthothricin

7-methoxyreumycin

One of the representatives of this group of antibiotics, namely reumycin, has been shown experimentally to exhibit a broad spectrum of antitumour activity.

The molecular mechanisms of the biological action and biotransformations of these compounds can be related to the intermediate formation of active free-radical states. Indeed, the formation of stable radical-anions from pyrimidotriazines during their electrochemical reduction has been demonstrated by EPR.[55] Microsomes, in which the reaction and detoxication systems of the xenobiotics are localised, can be used for the enzymic activation of pyrimidotriazines *in vitro*. It has been shown that the antibiotics of this series are capable of accepting an electron from the NADPH-cytochrome b_5 reductase chain.[56]

The reduction of reumycin in microsomes has been investigated in the presence of NADPH at different pH. When reumycin was reduced in an alkaline medium (the chemical reduction was carried out with potassium tetrahydroborate at pH 9.0, while the microsomal reduction was carried out at pH 8.0), the EPR spectrum consisted of an octet of lines with the constants $a^H = a^N = 5.7$ G for splitting due to the interaction with the three equivalent nitrogen atoms and the hydrogen atom of the triazine ring (Figs.13*a* and 13*b*).



Following the microsomal reduction of the methylated reumycin derivative, an analogous eight-component spectrum was recorded, whence it follows that the electronic structure and the distribution of spin density in the reumycin and 7-methoxyreumycin radical-anions are similar. Since reumycin ($pK_a \approx 6.5$) exists mainly in the anionic form at pH 8, presumably the anion undergoes one-electron reduction in the microsomes to a radical-dianion, which is capable of being rapidly protonated at the O(7) or the N(1) atom. However, one should note that the EPR spectrum of this radical differs from that of the radical-anion obtained on electrochemical reduction of 7-methoxyreumycin in dimethylformamide, which can be attributed to the conditions of its preparation in the aprotic medium.

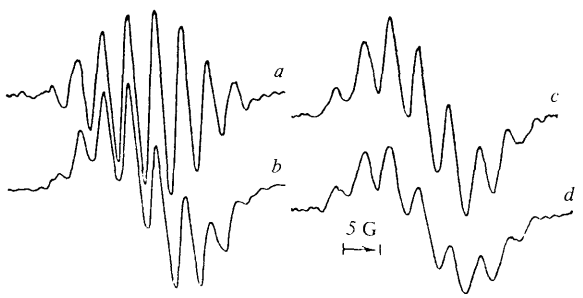


Figure 13. EPR spectra of reumycin radicals obtained under different conditions: *a*) on chemical reduction with KBH_4 at pH 9.0;[35] *b*) on microsomal reduction in the presence of NADPH at pH 8.0; *c*) on chemical reduction with KBH_4 at pH 4.0; *d*) on microsomal reduction in the presence of NADPH at pH 6.0.

In an acid medium, where unionised forms of reumycin are reduced (the chemical reduction is carried out at pH 4.0 and the enzymic reaction at pH 6.0), the character of the measured EPR spectra changes. Thus a seven-component EPR signal with constants for splitting (a = 5.6 G) by the three approximately equivalent nuclei of the nitrogen atoms in the triazine ring was obtained for the radical-anion (Figs.13*c* and 13*d*). On recording the spectra at a lower modulation amplitude, a finer structure due to the further splitting of the above seven lines was observed.

An analogous spectrum was recorded on microsomal reduction of fervenulin. The replacement of the hydrogen atom by the methyl fragment in the 8-position probably does not influence the character of the distribution of spin density in the radical-anions. Following the microsomal reduction of xanthothricin, a ten-component spectrum was obtained: this is also due to the splitting of the signal of the unpaired electron as a result of the interaction with the three equivalent nitrogen atoms and the three hydrogen atoms of the methyl group in the triazine fragment. The spin density in the pyrimidotriazine radical-anion is apparently localised mainly in the triazine ring. Thus in biological systems there is a possibility of the reduction of both reumycin and of its anion depending on the pH of the medium.[35]

In the general case the equation of the oxidation-reduction reactions in protic media can be written in the form

$$A + n e^- + m H^+ \rightleftarrows AH_m^{(n-m)-}.$$

For reversible processes, the potential of this system is described by the following expression according to the Nernst equation:

$$E = E_0^0 + \frac{RT}{nF} \ln \frac{[A]\,[H^+]^m}{[AH_m^{n-m}]}.$$

At a reduction half-wave potential $E_{1/2}$ such that the concentrations of the oxidised and reduced forms on the electrode surface are equal, the above equation can be put in the form

$$E_{1/2} \cong E^0 + \frac{RT}{nF} \ln [H^+]^m \cong E^0 - \frac{2.3mRT}{nF} \text{pH}$$

or

$$\Delta E_{1/2}/\Delta \text{pH} = -2.3 \frac{mRT}{nF}.$$

The overall dependence of $E_{1/2}$ on pH is represented by several straight lines having different slopes and the pH values at the break points correspond to the ionisation constants (pK_a) of the oxidised or reduced form. If the absolute value of $\Delta E_{1/2}/\Delta$pH, i.e. the slope of the straight line, beyond the break point decreases with increasing pH, then the break itself is due to the dissociation of the reduced form and the corresponding pK_a refers to the latter.[57]

Thus a comparative study of the rules governing the variation of the half-wave potential $E_{1/2}$ with the pH of the medium for two pyrimidotriazine antibiotics showed (Fig.14) that in the pH range 4–10 the dependence of $E_{1/2}$ on the pH for fervenulin, which is incapable of ionisation, consists of a straight line whose slope is −0.06. For reumycin, which is an acid (pK_a = 6.5), this relation has a more complex form with a characteristic break in the region where the pH approximately equals pK_a. As a result of this, reumycin is reduced less effectively in alkaline media and more effectively in acid media than fervenulin.

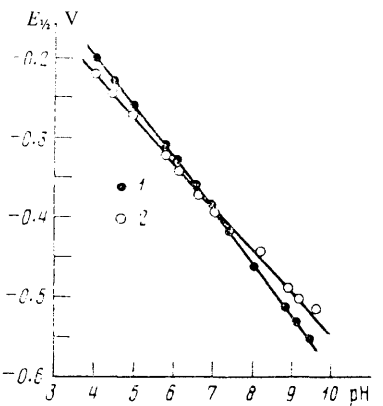


Figure 14. Dependence of $E_{1/2}$ for reumycin (line *1*) and fervenulin (line *2*) on pH.

The overall tendency towards an enhancement of the electron-accepting properties of the antitumour antibiotics with decrease of pH can be one of the causes of their selective action on tumour cells whose pH is lower than the normal value.

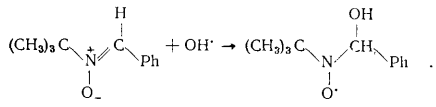
III. THE INTERACTION OF THE SEMIQUINONE RADICALS OF THE ANTIBIOTICS WITH INTRACELLULAR OXYGEN

The semiquinone radicals of antibiotics, formed during enzymic reduction, are destroyed under aerobic conditions on interaction with oxygen, forming the superoxide radical:

$$A^{\cdot-} + O_2 \overset{k}{\rightleftarrows} A + O_2^{\cdot-}$$

The rate constant for the generation of superoxide at pH 7 is higher than 10^8 litre mol^{-1}. This reaction is reversible, the rate of the reverse reaction being lower by two orders of magnitude.[29,58,59] According to the results of Chance et al,[60] the partial oxygen pressure is 7 mmHg (10 μM) in normally functioning cells *in vivo*. Assuming that the oxygen concentration is 10 μM and that $[O_2] \gg [O_2^{\cdot-}]$ (i.e. the reaction is of pseudofirst order), we find that the lifetime of the semiquinone radical *in vivo* is $\ln 2/k[O_2] = 6$ μs. Consequently the semiquinone radicals of antibiotics are unstable in normal cells and their chemical reactions (including the possible reactions with macromolecules) are very rapid. Naturally, in the presence of a reduced oxygen content (for example, in the cells of malignant tumours) the lifetime of semiquinone radicals can increase significantly, which entails an increase of the probability of free-radical reactions in the biotransformation of the antibiotic.

The detection of the formation of the $O_2^{\cdot-}$ and $OH^{\cdot}$ radical-ions is difficult owing to their high reactivity. One of the most convenient ways of detecting the formation of superoxide and hydroxy-radicals is the spin trapping method. N-t-Butyl-α-phenylnitrone (BPN) and 5,5'-dimethyl-1-pyrroline 1-oxide (DMPO) are most often used for this purpose. For example, when an aqueous solution of BPN in a phosphate buffer at pH 7 is added to a solution of the semiquinone radical in DMSO, obtained by the reduction of the AAA with KBH_4, a radical, which is a spin-adduct of BPN and the OH group of the semiquinone radical, is formed:



Its EPR spectrum consists of a doublet (a = 16.0 G) of triplets (a = 3.4 G) with g = 2.0061. When a solution of the semiquinone radicals of antibiotics was mixed with an aqueous solution of BPN containing catalase or superoxide dismutase (SOD), the formation of nitroxy-radicals was not observed.[39] On the other hand, the denatured forms of these enzymes no longer inhibited the formation of the BPN–OH nitroxy-radical spin-adducts. It has been shown for bruneomycin that in the presence of EDTA the spin-adducts are not formed, which indicates an important role of heavy metal ions in the generation of the $OH^{\cdot}$ radical-anions.[39]

Naturally the above spin-adducts are formed only in the presence of oxygen. For example, when adriamycin is incubated with microsomes, the formation of the DMPO–superoxide adduct is observed only when oxygen is present in the microsomes.[27] After the complete consumption of the oxygen dissolved in the incubation medium, the EPR signals of the spin-adducts of $OH^{\cdot}$ and $O_2^{\cdot-}$ disappear and the EPR signal of the semiquinone radical of adriamycin appears. At least two factors influence this phenomenon: firstly, the DMPO–superoxide adduct has a lifetime of 45 s at pH 7.4[27,61] and, since molecular oxygen is consumed, the formation of nitroxy-radicals can cease; secondly the spin-adduct is enzymically reduced, like other nitroxy-radicals.[27,62] On the basis of these features, the following sequence of reactions has been proposed:[33]

$$A + e^- \rightarrow A^{\cdot-},$$

$$A^{\cdot-} + O_2 \rightarrow A + O_2^{\cdot-}$$

$$2H^+ + 2O_2^{\cdot-} \xrightarrow{SOD} H_2O_2 + O_2,$$

$$2H_2O_2 \xrightarrow{catalase} 2H_2O + O_2,$$

$$M(II) + H_2O_2 \rightarrow M(III) + OH^{\cdot} + OH^-,$$

$$M(III) + O_2^{\cdot-} \rightarrow M(II) + O_2,$$

$$H_2O_2 + O_2^{\cdot-} \rightarrow OH^- + OH^{\cdot} + O_2,$$

Another way of detecting $O_2^{\cdot-}$ radical-ions in solution may be to determine the adrenochrome formed from adrenalin.[15] The rate of formation of superoxide radicals is estimated from the rate of oxidation of adrenalin and the formation of adrenochrome, which is determined spectrophotometrically from the absorption at a wavelength of 480 nm. The addition of superoxide dismutase (10 μg ml^{-1}) inhibits the formation of adrenochrome.

The generation of superoxide radicals by pyrimidotriazine antibiotics in rat liver microsomes has been investigated.[35] In the absence of NADPH, the rate of formation of $O_2^{\cdot-}$ in the microsomes is very low (w = 0.3 nmol per mg of protein per minute) and does not increase after the addition of reumycin, which is not reduced under these conditions to a radical-anion. In the presence of NADPH, the electron transfer from NADPH to oxygen with formation of superoxide radicals is observed (w = 1.8 nmol per mg of protein per minute). The addition of reumycin to the system increases sharply the rate of formation (w = 6.5 nmol per mg of protein per minute) of superoxide radicals (the formation of adrenochrome) owing to the transfer of an electron from the radical-anions of the antibiotic to oxygen. Under these conditions, the EPR spectra of the reumycin radical-anions were detected only after the complete consumption of oxygen. Xanthothricin, which has the lowest reduction potential,[55] is capable of being reduced in microsomes without the addition of NADPH. The radical-anions formed under these conditions generate superoxide radicals at the highest rate (w = 11.1 nmol per mg of protein per minute). This can probably explain the high toxicity of xanthothricin and its low chemotherapeutic index. This confirms the earlier hypothesis of the role of the stability of the intermediate active free-radical forms of the antitumour preparations in the selectivity of their action.[63]

Comparison of the properties of reumycin with those of other antibiotics of this series makes it possible to explain the higher selectivity of its antitumour action. In tumour cells, where the pH is reduced (6.5), the reumycin–reumycin anion equilibrium is displaced towards the unionised form. Owing to its low reduction potential, the neutral form of reumycin can oxidise a large number of enzyme systems with formation of highly reactive radical-anions and, by virtue of the causes stated above, this can lead to a pronounced cytotoxic activity. In normal cells, whose pH is 7.5, reumycin exists to the extent of 90% in the ionised form, whose capacity for reduction to radical-ions is much lower. This is in fact apparently the cause of the selectivity of the action of reumycin in relation to tumour cells.

The formation of superoxide and hydroxy-radicals as a result of electron transfer from the semiquinone radicals of antibiotics to oxygen has been established also for bruneomycin,[39] actinomycin D,[15] anthracycline antibiotics,[27] and mitomycin C.[27]

The formation of radicals from quinone-containing antibiotics and their subsequent destruction on interaction with oxygen can also be characterised by the degree of microsomal oxidation of NADPH and the consumption of oxygen.

Substances of the benzoanthraquinone class, *N*-heterocyclic quinones, and naphthcquinones stimulate the oxidation of NADPH but at different rates. Cytotoxic preparations (cyclophosphane, methotrexate, etc.) are inactive, which has been established by the quantitative analysis of the microsomal oxidation of NADPH (Table 7).[26]

Another index of the intensity of electron transfer from the antibiotic semiquinone to oxygen is the increase of the rate of consumption of oxygen. It has been observed that the rate of consumption of oxygen is proportional to the concentration of both the quinone-containing antibiotic and that of the enzymes. Antitumour preparations not containing quinone groups and not increasing the rate of microsomal oxidation of NADPH do not influence the consumption of oxygen by microsomes.[26,29] The highest rates of formation of superoxide radicals, estimated from the rate of consumption of oxygen in the presence of rubomycin, was reached at pH 7.8–8.4, although in phosphate buffer a higher rate was noted than in tris buffer. The consumption of oxygen stimulated by AAA was also sensitive to the concentration of the buffer; the maximum rate was attained in 0.2 M buffer.[29]

Table 8. Rates of consumption of oxygen by various subcellular extracts in the presence of rubomycin.[29]

Object	w_1, nmol/mg protein per min	w_2, nmol/mg protein per min
Cytoplasmic liver extract	0.3	1.6
Liver mitochrondria	2.1	4.3
Liver microsomes	25.2	93.0

Notation: w_1 and w_2 are the rates of the intrinsic and rubomycin-catalysed consumption of oxygen.

Various subcellular extracts stimulate the consumption of oxygen to different extents, which is due to the differences between the amounts of enzymes capable of catalysing the electron transfer from NADPH to the quinone-containing antibiotic (Table 8).[29] This process proceeds most vigorously in microsomes. At the same time the difference between the activities of microsomes from different organs is noteworthy. The microsomes of different organs (liver, lungs, and heart) of mice and rats have been investigated and their capacity to increase the consumption of O_2 has been determined using adriamycin as the substrate (Table 9).

It has been found that the microsomes from L-1210 and P-388 tumour cells also catalyse the increase of the consumption of oxygen but to a much lesser extent than the microsomes from the normal organs, which is due to the disturbance of the functional activity of tumour cells and cell organelles (Table 9).[26]

Table 9. Kinetic constants* for the consumption of oxygen stimulated by adriamycin.[26]

Microsomes	$10^4 K_m$, mol litre^{-1}	$10^7 V_{max}$, mol min^{-1}
Rat liver	3.6	0.92
Rat lungs	3.1	0.39
Rat heart	186.0	0.89
Mouse liver	8.0	2.6
Mouse lungs	2.4	0.44
Mouse heart	3.1	0.06
Mouse spleen	28.0	0.14
L-1210 cells	4.4	0.2
P-388 cells	0.6	0.04

*K_m and V_{max} are the parameters of the Michaelis equation.

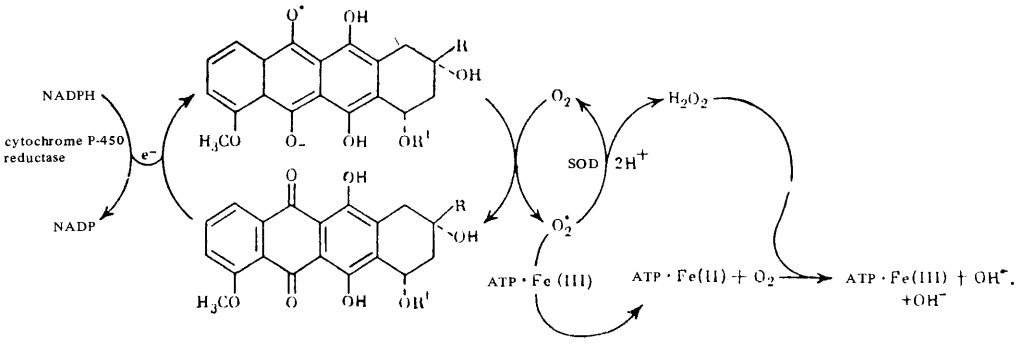
Table 10. Kinetic constants* for the consumption of oxygen stimulated by AAA in microsomes.[29]

Antibiotic	K_m, μmol litre^{-1}	V_{max}, nmol min^{-1}
Rubomycin	390	35
Adriamycin	260	240
Daunorubicinol	250	230
Carminomycin	110	770
Adriamycin Fe^{3+}	250	620

*K_m and V_{max} are the parameters of the Michaelis equation.

All the anthracycline antibiotics are capable of transferring an electron from NADPH to oxygen. Carminomycin is outstanding in this series, catalysing the electron transfer to oxygen at the highest rate; this property is correlated with its high toxicity (Table 10).[29]

In the general case the AAA and their structural analogues with an *N*-quinonoid fragment form semiquinone free radicals on reduction *in vivo*, their autoxidation resulting in the generation of superoxides.



According to the experimentally justified scheme presented above, antibiotics of this series act as competing agents for electron transfer to oxygen in the biological oxidation chain.[64] Naturally, chemical modification of the antibiotics, involving a decrease of their capacity to generate superoxides, should be accompanied by a decrease of toxicity. Indeed the monoxime of bruneomycin, which cannot function as an agent transferring electrons to oxygen, proved to be less toxic in relation to *E. coli* and the magnitude of the toxic dose was independent of the level of the superoxide dismutase activity of the cells.[65]

Various additives to microsomes can alter the consumption of oxygen. Thus coenzyme Q appreciably increases both the intrinsic and the rubomycin-stimulated consumption of oxygen. On the other hand, α-tocopherol, which is a familar natural antioxidant, inhibits the intrinsic consumption of oxygen by 60% and the antibiotic-stimulated consumption by 80%. On the other hand, glutathione and cysteine activate the consumption of oxygen (Table 11).[29]

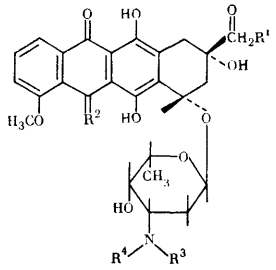
Table 11. The influence of various additives on the rate of consumption of oxygen by microsomes.[29]

additive	w_1, nmol O_2 min^{-1}	w_2, nmol O_2 min^{-1}
Without additive	35	296
Hexobarbital	88	309
Aspirin	54	302
Coenzyme Q	53	447
GSH	53	389
Cysteine	49	388
α-Tocopherol	13	68
EDTA	18	252
Fe^{3+}	49	315

Notation: w_1 and w_2 are the rates of the intrinsic and adriamycin-catalysed consumption of oxygen and GSH is reduced glutathione.

The main secondary effect of the AAA is cardiotoxicity. The relation between the cardiotoxicity in the series of AAA and the inhibition by the latter of the synthesis of cardiac guanylate cyclase has been investigated[66] and it has been observed that synthetic AAA containing hydrazone derivatives in the C(9)-position do not inhibit but actually stimulate the guanylate cyclase activity.

The cardiotoxocity has been explained recently by the formation of the O_2^- and $OH^\cdot$ radical species in the cardiac muscle. There is a correlation between the capacity to form superoxide radicals and the cardiotoxicity of certain anthracyclines[64] (Fig.15).



$R^1 = H$, $R^2 = NH$, $R^3 = H$, $R^4 = CH_2Ph$ (XVIII); $R^1 = H$, $R^2 = O$, $R^3 = R^4 = CH_2Ph$ (XIX); $R^1 = OH$, $R^2 = O$, $R^3 = R^4 = CH_3$ (XX).

The toxic activity of the radicals on cardiac muscle is associated with the reduced content of superoxide dismutase and catalase in the cell (Table 12).[34] It has been demonstrated *in vivo* that the introduction of the natural antioxidant α-tocopherol leads to a decrease of cardiotoxicity and an increase of the lifespan of animals.[67] It has been shown that ascorbate can also decrease the overall toxicity and cardiotoxicity of the preparations due to the AAA. Electron microscope and histological studies have demonstrated that ascorbate prevents the early changes in cardiac muscle under the influence of AAA.[68]

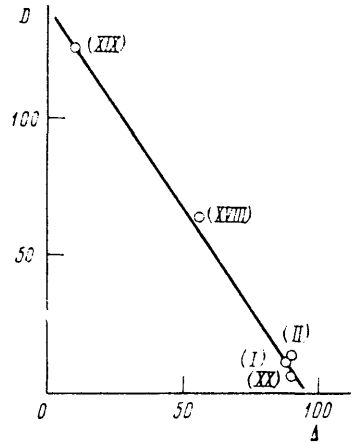


Figure 15. Relation between the dose of anthracyclines giving rise to the same Zbinden cardiotoxic effect (D) and the relative rate of generation of superoxide radicals by various anthracyclines (Δ) (according to the data of Lown et al.[64]

Table 12. The relative activities of catalase (in relative units) in various organs of the rat and rabbit.[34]

Organ	Rabbit	Rat
Blood	20	16.2
Liver	23	45.3
Kidneys	26	19.0
Lungs	2.9	1.9
Heart	1.0	1.0

It has been observed that AAA stimulate the peroxide oxidation of lipids. Incubation of rat liver microsomes with the NADPH-generating system produces approximately 10 nanoequivalents of malonaldehyde per mg of protein in 60 min. The peroxide oxidation was 6 times faster after the addition of 100 μM adriamycin. The AAA-stimulated peroxide oxidation of lipids influences the activity of certain enzyme systems of microsomes.[69] An 85% decrease of the content of cytochrome P-450 reductase and 70% inhibition of the activity of aminopyrine *N*-demethylase have been observed. The peroxide oxidation of lipids did not influence the NADPH-cytochrome *c* reductase activity; the UDP-glucuronyl transferase activity increases by a factor

of 5, while the glucose-6-phosphatase activity decreases by a factor of 6 under these conditions. In the absence of the peroxide oxidation of lipids, adriamycin also influences these enzymes[69] but to a lesser extent (Fig.16).

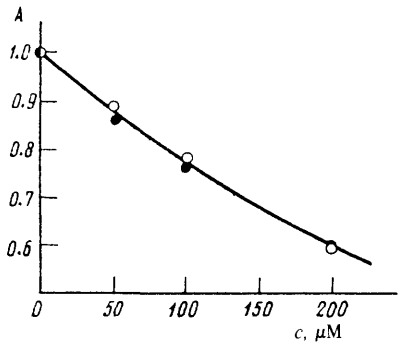


Figure 16. The influence of the concentration of adriamycin (c) on the content of cytochrome P-450 and the activity of aminopurine *N*-demethylase in the absence of the peroxide oxidation of lipids (according to the data of Mimnaugh et al).[69]

From the above, one can reach the following conclusions: both the anions and the radical-anions of the AAA can be oxidised in the organism, the toxic activity of the preparations is due to their capacity for oxidation, and the introduction of special antioxidants competing with the preparations is essential for the reduction of their toxicity.

In order to improve the antitumour index and reduce cardiotoxicity, various analogues of natural AAA have been synthesised. The introduction of the imino-group in the 5-position of the chromophore reduces the capacity for reduction and subsequent oxidation. This leads to a considerable decrease of the rate of generation of superoxide radicals compared with adriamycin.[55]

Changes in the carbohydrate ring can also influence the capacity of AAA for enzymic reduction. Thus *N*-methylation of the sugar group increases the capacity of AAA for reduction, the degree of consumption of oxygen, and the rate of formation of superoxide radicals. The cardiotoxicity of these preparations increases under these conditions.[64] If two *N*-benzyl groups are introduced into the carbohydrate fragment, then the consumption of oxygen and the formation of superoxide radicals diminish sharply. This can be associated with the steric inhibition of the action of the microsomal cytochrome P-450 on the antibiotic.

The activation of medicinal preparations and their subsequent metabolism depend on the functional state of the cells and the degree of their differentiation. The differences in the effectiveness of the action of particular antitumour antibiotics as a function of the degree of aeration of the tumour cells may be associated with this particular factor. In terms of this factor, the series of known carcinolytic substances can be divided into three groups, which are presented in Table 13.[70]

The group of preparations whose cytotoxic effect increases with increase of the concentration of oxygen includes three antibiotics: bleomycin, bruneomycin, and actinomycin D. It is known that bleomycin is characterised by high pulmonary toxicity, which increases significantly with increasing partial pressure of O_2.[71] Bleomycin causes ruptures in DNA molecules and its reactivity depends on the presence of iron ions and molecular oxygen. The highly reactive radical forms of oxygen can be responsible for the breaks in DNA under these conditions. It has been shown that the reaction of bleomycin with [^{3}H]DNA in the presence of iron ions is inhibited when the reaction mixture is bubbled with argon. On aeration, the reaction proceeds via the ternary complex O_2–Fe(II)–bleomycin [O_2–Fe(II)–B], whose properties are analogous to those of haem-containing oxygenases.[72] This complex is formed on direct oxidation with molecular oxygen of Fe(II)–bleomycin [Fe(II)–B], the second-order reaction rate constant amounting to $k = 6.1 \times 10^3$ mol^{-1} s^{-1}:

$$\left.\begin{matrix} O_2 \\ Fe(II)—B \end{matrix}\right\rangle \rightarrow O_2—Fe(II)—B \leftrightarrow O_2^{\cdot-}—Fe(III)—B \left\langle\begin{matrix} \rightarrow O_2^- \\ \rightarrow Fe(II)—B \end{matrix}\right.$$

The subsequent stage involving the generation of a superoxide radical with formation of the complex Fe(II)–B is characterised by the first-order rate constant $k = 0.12$ s^{-1}. At pH 7 the oxidation of the complex Fe(II)–B with oxygen leads to the formation of three different paramagnetic forms of Fe(III)–B: one high-spin form ($s = 5/2$) and two low-spin forms ($s = 1/2$). The low-spin form having the spectroscopic parameters $g_{xx} = 2.25$, $g_{yy} = 2.17$, and $g_{zz} = 1.94$ is unstable and disappears rapidly (after 60 s at room temperature). The other two forms, namely the high-spin form ($g = 4.3$) and the other low-spin form ($g_{xx} = 2.40$, $g_{yy} = 2.18$, and $g_{zz} = 1.90$), are stable.[73]

Table 13. Classification of the antitumour agents in terms of the effectiveness of their action as a function of the degree of aeration of the cells.[70]

Agents whose action depends on the degree of aeration		Preparations whose action is independent of the degree of aeration
active under aerobic conditions	active in hypoxia	
Bleomycin	Mitomycin C	5-Fluorouracil
Bruneomycin	Adriamycin	Methotrexate
Actinomycin D	Misonidazole	*cis*-Dichlorodiaminoplatinum
Procarbazine	Metronidazole	*N,N'*-Di(chloroethyl)-*N*-nitrosourea
Vincristine	5-Thio-D-glucose	
Ionising radiation	2-Deoxy-D-glucose	*N*-Chloroethyl-*N'*-cyclohexyl-*N*-nitrosourea

Under aerobic conditions, the reduction of bruneomycin with tetrahydroborate in the presence of DNA is accompanied by a decrease of viscosity and of the average molecular weight of DNA[44] owing to the appearance of single breaks in the DNA molecule.[74] Since superoxide dismutase inhibits this process,[75] presumably active radical forms of oxygen are responsible for the degradation of the DNA. These results make it possible to explain the enhancement of the toxic activity of bruneomycin on *E.coli* in the presence of oxygen or in the presence of a reduced SOD content.

Whereas the action of mitomycin C is determined by the alkylation of biomacromolecules and the formation of cross-links between them, the cytotoxic activity of bruneomycin is due to the active oxygen radicals. The selective action on tumour cells by preparations generating these radicals can be accounted for by the reduction of the SOD content in

tumour cells.[76] The selective increase of the O_2 concentration in tumour cells can apparently be used for the specific chemotherapy of tumours.

Yet another antibiotic of this type is actinomycin D. The mechanism of its action can be accounted for by its capacity for intercalation between the DNA bases.[38] At a concentration less than 0.01 μM, the difference between the cytotoxicities of this antibiotic under aerobic conditions and in hypoxia is small. However, at a concentration of approximately 1 μM, oxygen-rich cells are approximately 100 times more sensitive to the lethal action of actinomycin D than under the conditions of hypoxia.[70] There exists apparently an alternative oxygen-dependent mechanism of the cytotoxic action of actinomycin D where a part of it remains non-intercalated between the DNA bases at fairly high concentrations of the preparation. On incubation with microsomal proteins, actinomycin D forms a semiquinone free radical which stimulates the consumption of oxygen and the electron transfer to oxygen. When actinomycin D and its spin-labelled analogues are incubated with liver microsomes in the presence of NADPH, the rates of consumption of oxygen, of formation of superoxide, and of oxidation of adrenalin increase (Table 14).[15] Evidently the spin-labelled antibiotics stimulate the formation of superoxide radicals to a greater extent than does actinomycin D.

Table 14. The rates of consumption of oxygen (w_1) and formation of andrenochrome (w_2) from adrenalin in microsomes in the presence of actinomycin D and its spin-labelled analogues.[15]

Preparation	w_1, nmol/mg protein per min	w_2, nmol/mg protein per min
(V)	8.17	2.45
(VI)	18.37	4.66
(VII)	99.28	13.96
Control	7.23	1.29

The influence of the binding of the preparations to DNA on the generation of O_2^- has also been studied. After actinomycin D had been incubated with DNA, it lost entirely its capacity to generate superoxide. The incubation of the spin-labelled analogues (VI) and (VII) with DNA reduced the rate of consumption of oxygen by 71 and 50% respectively and also decreased the rate of oxidation of adrenalin. These results indicate yet again that the antibiotics intercalated between DNA bases are "poor" substrates for enzymic reduction. Thus the formation of superoxide, hydrogen peroxide, and hydroxy-radicals can play an important role in the antitumour activity of preparations of the type considered.[15]

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The set of data obtained permit a number of conclusions concerning the molecular mechanisms of the toxic and antitumour activities of the active free-radical forms of antibiotics. The demonstration of the formation of the chemically reactive forms of reduced oxygen and of the covalent binding of the free-radical forms of the antibiotics to biomacromolecules must be regarded as the most important of these.

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Division of the Institute of
Chemical Physics,
USSR Academy of Sciences,
Chernogolovka

Translated from *Uspekhi Khimii*, 53, 1959-1984 (1984) U.D.C. 535.3 + 541.6 + 547.024

The Vibrational Spectra of Neutral Free Radicals and the Corresponding Ions

L.A.Kotorlenko and V.S.Aleksandrova

The results of studies on the vibrational spectra of simple and polyatomic neutral free radicals and the corresponding ions—the products of the one-electron reduction or oxidation of these radicals—are analysed.
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I. INTRODUCTION

Many chemical reactions proceed via a free-radical mechanism. The kinetics of such reactions are usually studied by EPR, which makes it possible to follow the time course of the reaction. However, in many instances the radicals can react without the involvement of the unpaired electron, which makes it difficult to follow the reactions of the radicals using EPR spectra. In such cases a detailed study and interpretation of the vibrational spectra of the intermediate radicals are necessary. The results of such studies for neutral and charged radicals have been surveyed.[1]

The extensive published experimental data show that, depending on the nature of the reacting substances, the free radicals can manifest a dual reactivity: on interaction with reductants and oxidants, they can respectively accept and give up an electron to form an anion or cation. Ionic reactions are known to play a significant role in organic processes and the investigation of the structures of ionic species is therefore extremely important. In the present review the vibrational spectra of free radicals and the corresponding ions are compared and certain considerations are put forward concerning the changes in the structure of the species as a consequence of the loss or addition of an electron. The influence of the protonation of molecules related to the radicals on their structure and vibrational spectra is also analysed.

II. THE VIBRATIONAL SPECTRA OF SIMPLE FREE RADICALS AND THEIR IONS

Simple free radicals and ions are extremely unstable and their detection by vibrational spectroscopy therefore involves considerable difficulties. Most studies employ the method of matrix isolation, whereby it is possible to detect free radicals and ions. There exists also another possibility for the investigation of the vibrations of short-lived molecular systems—the high speed recording of spectra; however, in view of its technical complexity it has been much less used.

Non-empirical calculations of the potential curves for the ground and excited electronic states of the $OH^{\cdot}$ radical and the ground state of the OH^{+} cation have been carried out[2] by the method of configuration interaction using pseudo-natural orbitals in terms of the approximation of bound electron pairs. The results agree with the experimental values listed in Table 1.

Table 1. The vibrational spectra and geometrical parameters of a series of simple molecules, radicals, and ions.

Species	ν, cm^{-1}	r, Å	α, °	$10^{-2}F_r$, Nm^{-1}	Refs.
OH^-	3570	—	—	—	[3]
$OH^{\cdot}$	3567[a]	0.971	—	—	[2]
$(OH^{\cdot})^*$	2689[a]	1.004	—	—	[2]
OH^+	2955	1.029	—	—	[2]
H_2O	3657 (asym.); 3756 (sym.)	0.957	105.2	7.66	[9]
H_3O^+	2600 (asym.); 3200 (sym.)	1.011	110.4	4.03—3.96	[9, 10]
NH_2^-	—	1.032	102.4	5.82	[17, 18]
$NH_2^{\cdot}$	3220	1.024	103.3	5.61	[11—14]
$(NH_2^{\cdot})^*$	3325	0.975	180	—	[13]
NH_2^+	2721 (asym.); 2822 (sym.)	1.03	108.7	4.68	[15, 16]
NH_3	3336 (asym.); 3414 (sym.)	1.017	107.8	6.16	[13, 16, 19]
NH_4^+	3040 (asym.); 3145 (sym.)	—	109.5	5.42	[17, 19]
PH_2^-	—	1.466	93.7	3.40	[24]
$PH_2^{\cdot}$	2270±80	1.442	94.6	7.26	[20, 23, 24]
PH_2^+	—	1.419	120.5	7.90	[24]
NO^-	1355[b]	1.286	—	—	[32]
$NO^{\cdot}$	1876[b]	1.151	—	—	[25, 27]
NO^+	2220; 2320—2340	1.062	—	—	[27—31]
NO_2^-	1315 (asym.); 1182 (sym.)	—	109	—	[33—35]
$NO_2^{\cdot}$	1329 (asym.); 1633 (sym.)	—	140.9; 126.1	—	[36—38]
NO_2^+	1400 (asym.); 2360 (sym.)	—	180	—	[19]
$NS^{\cdot}$	1210	1.469	—	10.33	[41, 45, 46]
NS^+	1415	1.439	—	12.65	[41, 44, 45]
PO^-	1000	1.540	—	—	[23]
$PO^{\cdot}$	1218	1.476	—	—	[47]
ClO^-	713	—	—	3.3	[83]
$ClO^{\cdot}$	850	—	—	4.66	[83]
ClO_2^-	789.7 (asym.); 823.4 (sym.)	1.57	108.5	4.11	[77, 80]
$ClO_2^{\cdot}$	947.6 (asym.); 1104.5 (sym.)	1.472	112.2	6.61	[77, 79]
ClO_3^-	936	1.46	108	6.62	[78, 81]
$ClO_3^{\cdot}$	855 (asym.); 815 (sym.)	—	110; 112	—	[81]

Notation: ν is the vibration frequency, r is the equilibrium distance, α the angle between the bonds, F_r the force constant, ω_e the normal vibration frequency for infinitesimal amplitudes, and $\omega_e\chi_e$ the anharmonicity constant. The asterisk denotes excited states.

[a] Obtained from $\omega_e = 3740\ cm^{-1}$, $\omega_e\chi_e = 86.4\ cm^{-1}$ and $\omega_e = 3181\ cm^{-1}$, $\omega_e\chi_e = 95.9\ cm^{-1}$ for $OH^{\cdot}$ and $(OH^{\cdot})^*$ respectively.[2]

[b] Calculated from $\omega_e = 1904\ cm^{-1}$, $\omega_e\chi_e = 14\ cm^{-1}$ and $\omega_e = 1371\ cm^{-1}$, $2\omega_e\chi_e = 16\ cm^{-1}$ for $NO^{\cdot}$ and NO^- respectively.[27,32]

From the analysis of the literature data on the infrared and Raman spectra of the hydroxides MOH (M = Li, Na, Rb, or Cs) and $M(OH)_2$ (M = Mg, Ca, Sr, or Ba) as well as their hydrates at 95 and 295 K, Lutz et al.[3] concluded that the frequency of the stretching vibration of the unperturbed OH^- ion is 3570 ± 10 cm^{-1}. This value differs appreciably from that usually adopted (3700 cm^{-1}). The formation of the cation decreases the vibration frequency of the O–H bond, while the latter hardly changes on formation of the anion. Since the OH^+ cation has a triplet ground state,[2] i.e. its formation involves the abstraction of an electron from the unshared pair, the observed weakening of the bond is due to the displacement of electron density from the bond to the oxygen atom. At the same time the vibration frequencies of the OH^- anion and the OH· radical are identical, which suggests that the electron which reduces the radical to the anion occupies a non-bonding orbital.

The infrared and Raman spectra of the oxonium ion H_3O^+ have been studied in a number of investigations.[4–8] The following assignment of the frequencies in the spectrum of the H_3O^+ ion has been adopted assuming a symmetrical pyrimidal structure: the symmetrical deformation (ν_2) at 1100 cm^{-1}, the antisymmetric deformation (ν_4) at 1700 cm^{-1}, the antisymmetric stretch (ν_3) at 2400 cm^{-1}, and the symmetrical stretch (ν_1) at 3200 cm^{-1}. The constants calculated using the valence bond approximation[9] describe satisfactorily the experimental data. The significantly lower force constant of the O–H bond in H_3O^+ compared with the value obtained in terms of the same approximation for H_2O (Table 1) is associated with the increase of the interatomic distance by 0.054 Å as a consequence of the shift of electron density to the O–H bond newly formed on protonation of the water molecule. On the basis of the analogous change in the equilibrium distance by 0.055 Å in OH^+ relative to OH·, a similar change in the force constant may be expected also on formation of the OH^+ cation from the OH· radical.

Milligan and Jacox[11] were able to obtain the most complete vibrational spectrum of the $NH_2^·$ radical. The band at 1499 cm^{-1} was assigned to the ν_2 deformation, while that at 3220 cm^{-1} was assigned to the ν_3 antisymmetric stretch. In the study of the fluorescence excitation spectrum of the $NH_2^·$ radical the band at 3219 cm^{-1} was assigned[12] to the ν_1 symmetrical stretch. The experimental value of ν_2 for the deuterio-analogue is 1110 cm^{-1}. According to the authors,[11] the 16 cm^{-1} hypsochromic shift of the experimental deformation vibration frequency of $ND_2^·$ relative to the calculated value is caused by the difference between the contributions of the anharmonicity to the potential energies of the $NH_2^·$ and $ND_2^·$ radicals.

The excitation of the $NH_2^·$ radical is accompanied by a considerable increase of the angle α and a decrease of the bond length (Table 1). These changes are caused by the *sp* hybridisation of the N–H bond in the excited state, while in the ground state the N–H bond has a predominantly *p* character with a small contribution of the *s* orbital.[11] On ionisation of the $NH_2^·$ radical, the valence angle increases[15] as on its excitation, according to Milligan and Jacox,[11] this should be accompanied by a decrease of the bond length. However, the presence of the positive charge localised at the nitrogen atom apparently shifts the electron density from the bond to the N atom and lengthens the bond. There are no experimental literature data for the geometry of NH_2^+, but the results of a calculation[15] (Table 1) confirm the view that these competing effects exist. On protonation of the NH_3 molecule, the valence force constant of the N–H bond diminishes compared with the initial molecule (Table 1), while the deformation force constant hardly changes.[17] A significant difference between the frequencies of the deformation vibrations of ammonia (ν_2 = 930–970 cm^{-1} and ν_4 = 1628 cm^{-1})[19] and its protonated form (ν_2 = 1680 cm^{-1} and ν_4 = 1400 cm^{-1})[19] is then observed. A characteristic feature is that the homolytic rupture of the bond in both NH_3 and in H_2O (with formation of the radical) is accompanied by a lengthening of the corresponding bond and hence by its weakening compared with the initial molecule.

The deformation vibration frequency in the ground electronic state $^2B_1$ of the $PH_2^·$ radical is 1102 cm^{-1},[20] which agrees with the values quoted by Dixon et al.[21] and Berthou et al.[22] The stretching vibration frequency of $PH_2^·$ [20,23] and the equilibrium distances, angles, and force constants of the radical and the corresponding ions, calculated[24] by the non-empirical SCF LCAO MO method, are listed in Table 1. Analysis[23] of photoelectron spectroscopic data led to the conclusion that the geometry changes insignificantly following the abstraction of an electron from the PH_2^- anion, which agrees with other results.[24] The decrease of the force constant of the P–H bond in the sequence cation > radical > anion is apparently caused by the antibonding character of the successively added electrons.

Taking into account configuration interaction, calculations have been carried out by the SCF LCAO MO method for the three ($^2\Pi$) states of the NO· radical and the 19 ($^{1,3}\Sigma$, $^{1,3}\Pi$, and $^{1,3}\Delta$) states of the NO^+ ion.[25] The calculated vibration frequencies in the ground state are 1731 cm^{-1} for the radical ($^2\Pi$) and 1515 cm^{-1} for the cation ($^1\Sigma^+$). The experimental frequencies and equilibrium distances for the NO· radical and its ions are listed in Table 1. Evidently the calculated value for the radical is too low by 10% and that for the cation is too low by 30–35%. On the basis of the experimental data (despite the fact that a fairly considerable scatter of the vibration frequencies has been observed for the cation), one can conclude that the formation of NO^+ and NO· entails the abstraction of an electron occupying an antibonding orbital; in contrast to calculated data,[25] this should be accompanied by a significant increase of the frequency. The character and magnitude of the change in frequency on reduction of the radical show that the added electron is also in an antibonding orbital but a different one, because NO^- has a triplet ground electronic state.[32]

Table 1 lists the stretching vibration frequencies of the nitrite anion NO_2^- and the corresponding radical and cation. The antisymmetric stretching vibration band of the anion[33] is a doublet due to the Fermi resonance of the ν_1 vibration with the combination $\nu_3 + \nu_C(B_1)$, where $\nu_C(B_1)$ represents the libration of the anion. We may also note that the vibration frequencies of the $NO_2^·$ radical in the gaseous state[36] and in an argon matrix[37] are virtually identical and are satisfactorily described by the calculated data.[38] The significant decrease of the symmetrical stretching vibration frequencies in the cation–radical–anion series is associated, as in the previous case, with the antibonding character of the added electrons. Consequently the reduction and oxidation of the radical are apparently accompanied by a change in geometry. Indeed, the O–N–O angles have been determined[34] on the basis of the isotope shifts with respect to oxygen and nitrogen for $NO_2^·$ and with respect to oxygen for NO_2^- (Table 1). Evidently the formation of the anion entails a change in the hybridisation of the N–O bond from sp^2 to sp^3. Whereas both the anion and the radical have a bent conformation, the cation has a linear geometry,[19] which indicates *sp* hybridisation of the N–O bond, the existence of the cumulated bond system $O{-}\overset{+}{N}{-}O$, and the localisation of the positive charge at the nitrogen atom.

Using a gas cell with multiple reflection, ensuring a beam path length of 80 m, an infrared band at 1360 cm^{-1} has been obtained[39] and interpreted as due to the antisymmetric stretching vibration of the $NO_3^·$ radical. Having measured

the Raman spectra of the substances obtained on condensation of the NO_2–N_2O_4–Ne gas mixture onto a copper support at 9 K, Griffiths et al.[30] assigned the 1042, 1324, and 714 cm^{-1} bands respectively to the ν_1, ν_3, and ν_4 vibrations of the NO_2^- anion isolated in a neon matrix. These frequencies are close to the corresponding vibration frequencies of the nitrate anion in HNO_3 [39] and $M^+NO_3^-$.[40] Comparison of the above data suggests that the antisymmetric stretching vibrations of $NO_3^{\cdot}$ and NO_3^-, like those of $NO_2^{\cdot}$ and NO_2^- (Table 1), are insensitive to changes induced by the one-electron reduction of the radicals.

The results of non-empirical calculations of the geometry and force constants of $NS^{\cdot}$ and NS^+ in the ground state by the restricted SCF method are also presented in Table 1. For the radical, they agree well with the experimental data.[42] In the case of the cation the calculated equilibrium distance differs significantly from the value of 1.25 Å found[43] from the emission spectra. It has been suggested[41] that the experimental estimate of r_e(N–S) for the cation is too low. The observed higher vibration frequency of the bond in $NS^{\cdot}$ [44] compared with the radical,[45,46] as in the case of $NO^{\cdot}$ and NO^+, indicates the removal of the electron from an antibonding orbital.

The changes in the vibration frequency and equilibrium distance on one-electron reduction of the $PO^{\cdot}$ radical[47,48] are listed in Table 1. The similarity of the vibration frequency of the $PO^{\cdot}$ radical to that of the stretch of the P–O bond in HPO (1188 cm^{-1}) indicates the localisation of the unpaired electron mainly at the phosphorus atom. The addition of an electron to the radical leads to a considerable decrease of the bond vibration frequency, caused, as in the case of $NO^{\cdot}$, by the concentration of the negative charge on the oxygen atom. The observed change in the vibrational spectrum is due to the increase of the equilibrium distance in PO^- compared with the radical.

The fluorescence and excitation spectra of the $NCO^{\cdot-}$ radical-ion isolated in an argon matrix have been obtained with the aid of a dye-based laser[48] (Table 2). The vibration frequencies ν_1 and ν_3 obtained agree well with infrared spectroscopic data,[49] while the frequency ν_2 proved to be higher by 42 cm^{-1}. The authors[48] indicated the presence of Fermi resonance between the ν_1 and $2\nu_2$ levels in the excited electronic state of $N\dot{C}O$. The reduction of the radical to the anion weakens the C–O bond (the ν_1 vibration) and strengthens the N–C bond (the ν_3 vibration) owing to the localisation of the negative charge on the oxygen atom. There are no experimental literature data for the vibrational spectra of the NCO^+ ion, while according to data calculated[53] by the SCF method for the NCO^+ linear system, the formation of the cation entails a decrease of the C–O internuclear distance and an increase of the N–C distance (Table 2). Since the cation has a triplet ground state,[53] its formation apparently involves the abstraction of an electron from the unshared electron pair of the nitrogen atom. The consequent presence of a positive charge on the nitrogen atom shifts the electron density from the bond to the nitrogen atom and lengthens the bond.

Table 2 presents the equilibrium distances and the frequencies and force constants for the $CN^{\cdot}$ radical and its ions. Analysis of the changes in the σ- and π-overlap energies[55] shows that the abstraction of an electron from the anion leads to the stabilisation of the σ-binding ($\Delta\Omega^{\sigma} = -0.40$) and to destabilisation of the π-binding ($\Delta\Omega^{\pi} = 0.57$), the influence of the latter effect being greater. According to the results of non-empirical calculations,[58] the CN^+ ion also has a triplet ground electronic state, which is indicated likewise by the character of the change in the equilibrium distance when the radical is converted into the cation. Presumably the vibration frequency of the cation is somewhat lower than that of the radical in the excited state.

The vibrational spectra of hydrogen dihalide free radicals (with $D_{\infty h}$ symmetry) and the corresponding anions have been investigated[59–65] (Table 3). In their study of the infrared spectra of the products, isolated in an argon matrix, of the interaction of Hal_2 and HHal (where Hal = Cl, Br, or I) in a discharge, Noble and co-workers[59–61] observed bands which were assigned to the ν_{sym} and ν_{asym} vibrations of the radicals $HHal_2^{\cdot}$ and $DHal_2^{\cdot}$. The presence in the spectrum of combined stretching vibration frequencies justifies the assumption that the anharmonicity of the bond vibrations is significant for the systems investigated. Indeed, the expressions for the potential energy of radicals of the type $HHal_2^{\cdot}$ include a large quartic term, which is responsible for the anharmonicity of the H–Hal bond vibrations, the contribution of the term diminishing sharply with increase of the size of the halogen atom.

Table 2. The spectroscopic characteristics and equilibrium distances of cyanate and cyanide ions and radicals.

Species	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	r_{CO}, Å	r_{NC}, Å	$10^{-2}F_r$, Nm^{-1}	Refs.
NCO^-	1210	627	2176	1.23	1.17	—	[50–52]
$NCO^{\cdot}$	1272	529	1923	1.18	1.23	—	[48]
NCO^+	—	—	—	1.125	1.468	—	[49]
NC^-	—	—	2080	—	1.14	16.4	[56, 57]
$NC^{\cdot}$	—	—	2042[a]	—	1.172	15.9	[54, 55]
$(NC^{\cdot})^*$	—	—	1788[a]	—	1.23	—	[54]
NC^+	—	—	—	—	1.27	—	[58]

[a] Obtained from $\omega_e = 2068$ cm^{-1}, $\omega_e\chi_e = 13$ cm^{-1} and $\omega_e = 1813$ cm^{-1}, $\omega_e\chi_e = 13$ cm^{-1} for $NC^{\cdot}$ and $(NC^{\cdot})^*$ respectively.

Analysis of the infrared and Raman spectra of HCl_2^- [62] and HBr_2^- [63] indicates a linear and centrosymmetric structure of the anions. The force constants obtained from the experimental data indicate insignificant changes in the force field following the abstraction of an electron from the non-bonding molecular orbital of the ions investigated. Comparison of the force constants for the $HHal_2^{\cdot}$–$HHal_2^-$ pairs leads to the conclusion that the contribution of the anharmonic term to the expression for potential energy is greater for the radical. The dependence of the contribution of this term on the size of the halogen atom for the ions is the same as for the radicals, but it is smoother. Thus the one-electron reduction of radicals of the type $HHal_2^{\cdot}$ has little influence on the strength of the hydrogen bond, but leads to an increase of the anharmonic character of the potential function. On the grounds that the HF_2^- spectrum is characterised by the vibration frequencies $\nu_{asym} = 600\,cm^{-1}$ and $\nu_{sym} = 1450\,cm^{-1}$ [64] or $\nu_{sym} = 1377$ cm^{-1},[65] Noble and co-workers[60] therefore suggest, in contrast to the calculated data,[66] that the radical $HF_2^{\cdot}$ should be stable.

The interaction of atomic fluorine with CF_2 in an argon matrix at 14 K made it possible[67] to obtain a concentration of the $CF_3^{\cdot}$ radicals sufficient (in contrast to another study[68]) for the detection of all four vibrations. This radical has the C_{3v} symmetry; its stretching vibration frequencies are listed in Table 3. On the basis of the results of the calculation, the authors[67] concluded that there is a Fermi resonance between the $\nu_2 + \nu_4$ and ν_3 vibrations in the $^{13}CF_3^{\cdot}$ spectrum and the force field parameters obtained indicate a pyramidal form for this radical. The angle of deviation from the plane is 13°, which has been confirmed by EPR data.[69]

Among the products of the photoionisation of CF_3X (where X = Cl, Br, I, or H), stabilised cations, previously detected (from the mass spectra) only in the gas phase, have been found in solid argon (Table 3).[70] The formation of these ions is accompanied by an increase in the frequencies of both the symmetrical and asymmetrical stretching vibrations. Particular mention should be made of the high antisymmetric stretching vibration frequency of the CF_3^+ cation due to the intense $(p-p)\pi$ interaction. On this basis, it has been concluded[70] that the difficulty of the stabilisation of the cation is caused by its high reactivity and not its "physical" instability. The low frequency of the experimental ν_{asym} band for the $^{13}CF_3^+$ cation compared with the calculated value (1612 cm^{-1}) has been explained[70] by the Fermi resonance between the $\nu_1 + \nu_4$ and ν_3 vibrations.

Table 3. Parameters of the infrared spectra of halogen-containing radicals and their ions.

Species	ν_{sym}, cm^{-1}	ν_{asym}, cm^{-1}	ν (C-X), cm^{-1}	Refs.
HCl_2^-	770	253	—	[62]
$HCl_2^{\cdot}$	696	260	—	[59]
DCl_2^-	520	225	—	[62]
$DCl_2^{\cdot}$	463.7	265.2	—	[59]
HBr_2^-	670	170	—	[63]
$HBr_2^{\cdot}$	727.4	164.7	—	[60]
DBr_2^-	550	160	—	[63]
$DBr_2^{\cdot}$	469.1	169.6	—	[60]
$HI_2^{\cdot}$	682.1	120.7	—	[61]
$DI_2^{\cdot}$	470	124	—	[61]
$CF_3^{\cdot}$	1087	1251	—	[67]
CF_3^-	1125	1667	—	[70]
$^{13}CF_3^{\cdot}$	1063	1219	—	[67]
$^{13}CF_3^+$	—	1600	—	[70]
$CF_2Cl^{\cdot}$	1208	1148	761	[70]
CF_2Cl^+	1515	1415	—	[70]
$CF_2Br_2^{\cdot}$	1197	1137	685	[70]
$CF_2Br_2^+$	1484	1368	—	[70]
$CF_2I^{\cdot}$	1190	1126	627	[70]
CF_2I^+	1433	1321	—	[70]
CF_4	908	1280	—	[19]

Since only the intense antisymmetric stretching vibration band is manifested in the infrared spectrum of the radical $CCl_3^{\cdot}$ [71] (Table 4) and the symmetrical stretching vibration band is absent, it has been suggested[72] that the radical has a planar structure (D_{3h} symmetry). However, the results of a non-empirical calculation[73] and EPR data[74] indicate a pyramidal structure. Table 4 lists the force constants for both the planar and pyramidal structures. On irradiation (λ = 1216 Å) of chloroform molecules isolated in an argon matrix at 14 K, CCl_3^+ cations have been obtained at a concentration sufficient for the investigation of their infrared spectra [72] (Table 4). The decrease of the force constant on passing from the cation to the radical demonstrates, as for $CF_3^{\cdot}$, the antibonding character of the unpaired electron. It is of interest to note that in the case of the CCl_4 molecule a further decrease of the antisymmetric stretching vibration frequency (force constant) and an increase of the deformation vibration frequency take place (Table 4).

Carver and Andrews[75] carried out the simultaneous deposition of chloroform and lithium vapour onto caesium iodide windows at high dilution in argon at 15 K and obtained bands in the spectrum of the product which were assigned to $HCCl_2^{\cdot}$ vibrations (Table 4). Postulating, by analogy with radicals of the type $CHal_3^{\cdot}$, that the unpaired electron in $HCCl_2^{\cdot}$ promotes the formation of a pyramidal structure, the authors[75] assumed that the H–C–Cl and Cl–C–Cl angles are 115°. The infrared spectra of matrix-isolated ions corresponding to the $HCCl_2^{\cdot}$ radical have been investigated.[72] A planar structure (C_{2v} symmetry) in the ground electronic state has been proposed for the $HCCl_2^+$ cation, as in the case of CCl_3^+. The addition of an electron to the $HCCl_2^{\cdot}$ radical leads to the formation of the anion $HCCl_2^-$, which has a pyramidal structure with still smaller valence angles. As for the isoelectronic H_2CCl_2 molecule, the angles in the anion are therefore assumed to be tetrahedral. The valence and deformation force constants obtained from these data are listed in Table 4. Evidently the force constant of the C–Cl bond gradually diminishes as each succeeding electron is added, which corresponds to a decrease of the strength and an increase of the length of the bond (from 1.70 Å for the cation to 1.75 Å for the anion). The deformation force constant depends on the valence angle, while the interaction constant hardly changes in the cation–radical–anion series.

Table 4. Parameters of the infrared spectra and force constants of certain chloro- and bromo-methanes.

Species	ν_{asym} (C-Hal), cm^{-1}	δ, cm^{-1}	α, °	$10^{-2}F_r$, Nm^{-1}	$10^{-2}F_\alpha$, Nm^{-1}	Refs.
$CCl_3^{\cdot}$	898	200*	116	3.1; 3.4	—	[71, 74]
CCl_3^+	1037	150–200*	120	3.8–3.9	—	[72]
CCl_4	790	314	109.5	3.08	—	[75]
$HCCl_2^-$	837.6	1270	109.5	3.27	0.76	[72]
$HCCl_2^{\cdot}$	902	1226	115; 120	3.75; 3.48	0.64; 0.48	[72, 75]
$HCCl_2^+$	1038	1291	120	4.65	0.52	[72]
$CBr_3^{\cdot}$	773	—	—	3.55	—	[76]
CBr_3^+	874	—	—	—	—	[65]
CBr_4	675	—	—	2.45	—	[76]

Notation: δ is the deformation vibration frequency and F_α the deformation vibration force constant; the remaining notation is the same as in Table 1.
*Postulated deformation vibration frequencies.

The formation of the tribromomethyl cation induces, as for CCl_3^+, an increase of the antisymmetric stretching vibration frequency (Table 4) compared with the radical. Whereas the frequency change for the trichloromethyl and tribromomethyl cations is 100–150 cm^{-1}, the corresponding value for the trifluoromethyl cation under these conditions (Table 3) is 400 cm^{-1}. The greater amount of double bond character in the $CCl_3^{\cdot}$ and $CBr_3^{\cdot}$ radicals relative to CCl_4 and CBr_4 is associated, according to the authors,[75,76] with the $(p-d)\pi$ interaction, the strength of which increases greatly for planar structures, i.e. for cations. On the other hand, following the homolytic dissociation of the C–F bond in CF_4, the asymmetric stretching vibration band (Table 3) undergoes a bathochromic shift, in contrast to $CCl_3^{\cdot}$ and $CBr_3^{\cdot}$, apparently owing to the absence of *d* orbitals.

Tevault et al.[77] investigated the infrared and Raman spectra and determined the parameters of the force field of the chlorite anion ClO_2^- and the corresponding $ClO^{\cdot}$ radical (Table 1). The calculated force constant of the Cl–O bond for the anion is much smaller than for the radical. The

results of a calculation[78] by the LCAO MO method, including the 3*d* orbitals of chlorine, predict for $ClO_2^{\cdot}$ that the π-bond order of the bond having 50% *d* character is 0.75, while that of the bond having total *d* character in ClO_2^- is 0.13. The higher π-bond order in $ClO_2^{\cdot}$ agrees with the greater bond force constant. Bearing in mind that only the *p* orbitals of the atoms are involved in the formation of molecular orbitals, one may conclude that the electron adding to the radical in the anion should occupy an antibonding molecular orbital which diminishes the $(p-p)\pi$ bond order. Both the lower valence force constant in the anion and the greater bond length agree with the antibonding character of the added electron. Tevault et al.[77] calculated the change in the O–Cl–O angle (Table 1) from the shift of the symmetrical stretching vibration frequency on isotope substitution of ^{35}Cl by ^{37}Cl, the result agreeing with the values found in other studies.[79,80]

The resonance Raman scattering (λ_{exc} = 6328 and 5145 Å) and the infrared spectra of the $ClO_3^{\cdot}$ radical formed on irradiation of $NaClO_3$ crystals by electrons having an energy of 15 MeV (T = 77 K) have been investigated[81] (Table 1). It was observed that the radical in the $NaClO_3$ lattice occupies two translationally non-equivalent positions, which leads to the splitting of the observed bands ($\Delta\nu$ = 5–7 cm^{-1}). Apart from the frequencies assigned to the vibration of the $^{35}ClO_3^{\cdot}$ radical, a band is shown in the infrared spectrum, which can be assigned to the ν_{sym} vibration of the $^{37}ClO_3^{\cdot}$ radical. However, the O–Cl–O angle obtained on this basis, which amounts to 100°, is lower than the value (112°) calculated from the EPR spectra.[82] The band at 936 cm^{-1} has been attributed to the symmetric ClO_3^- vibration, which is consistent with other data.[19] The anion under consideration has a pyramidal structure; its geometrical parameters and the valence force constants are given in Table 1. According to Wagner,[78] the ClO_3^- anion is characterised by a Cl–O bond whose π-bond order is 0.28 and which is fully of the *d* type.

In the photolysis of a Cl_2–O_2 mixture the infrared spectrum of the products showed (a multireflection gas cell with an optical length of 80 m was used) a band at 942 cm^{-1}, which was assigned[83] to the vibration of the short-lived $ClO^{\cdot}$ radical. This value is close to that (Table 1) obtained from the Raman spectra of the $ClO^{\cdot}$ radical isolated in the argon matrix. The vibrational frequency (850–1030 cm^{-1}) and force constants [$(4.8–6.9) \times 10^2$ N m^{-1}] for this radical has been calculated[78] by the method of "atoms in the molecule". The low vibrational frequency of the ClO^- anion (Table 1) indicates the localisation of the negative charge on the oxygen atom, which is confirmed by the absence of a π-component of the bond in it.[78] On the other hand, the radical has a π-bond order of 0.5 (a bond having 100% *p* character). The involvement of the *d* orbital, responsible for the electron-accepting properties, increases in the sequence[78]

$$ClO^- < ClO^{\cdot} < ClO_2^- < ClO_2^{\cdot} < ClO_3^- < ClO_4^-$$

In analysing this sequence, one can assume that the electron-accepting capacity of $ClO_3^{\cdot}$ is greater than that of ClO_3^-. However, sometimes (and the antibonding character of the outer molecular orbital of the systems of the type ClO_n considered agrees with this) the stretching vibration frequencies of the $ClO_3^{\cdot}$ radical should appear in a higher range than those of its anion. This conflicts with the results of Bates and Stidham.[81] The discrepancy with these data can be accounted for by the influence of the crystal field of $NaClO_3$, whose effect is apparently different for the radical and the anion.

The vibrational spectra of the methyl radical $CH_3^{\cdot}$ both in solid inert gas matrices and in the gaseous state have been investigated in a number of studies.[84–87] The most complete infrared spectrum has been described by Snelson[84] (Table 5). A stretching vibration frequency ν_1, not shown in the infrared spectrum, has been predicted. The force field parameters obtained for the radical agree well with the experimental data. The discrepancy between the calculated and experimental frequencies for $CD_3^{\cdot}$ is due to the influence of the anharmonicity[84] and is not a result of the interaction of the radical with the matrix. In the ground electrostatic state the methyl radical has a planar[85,86] or quasi-planar[88] structure.

The methyl anion CH_3^- has been generated in the gas phase; its photoelectron spectrum has been obtained with a well resolved vibrational structure, whereby it is possible to determine the deformation vibration (umbrella motion) frequency[88] (Table 5). It was concluded that the CH_3^- anion has a pyramidal structure, which agrees with data for anions of the type $CHal_3^-$. The methyl cation CH_3^+ has a planar structure and the equilibrium distance (Table 5) suggests that its stretching vibration frequencies should have undergone bathochromic shift compared with the radical and should appear close to the stretching vibrations of methane.

Table 5. Parameters of the infrared spectra and equilibrium distances in the molecules of methane and its derivatives.

Species	ν_1, cm^{-1}	δ_2, cm^{-1}	ν_3, cm^{-1}	δ_4, cm^{-1}	*r*, Å	Refs.
CH_3^-	—	460	—	—	—	[88]
$CH_3^{\cdot}$	3044	617	3162	1398	1.079	[84–86, 88]
$CD_3^{\cdot}$	2153	463	2381	1026	—	[84]
CH_3^+	—	—	—	—	1.091; 1.120	[90, 91]
CH_4	2916	—	3019	—	1.094	[89]

A series of studies of the structure and infrared spectra of alkyl radicals merit attention.[92–95,105,109] Pacansky and Dupuis[93] investigated the vibrations of the bonds and angles in the ethane–ethyl radical–ethylene series, which enabled them to interpret the infrared spectrum of the ethyl radical and its deuterio-analogue. The geometrical parameters calculated by the non-empirical SCF method were used in the calculation. The infrared bands of the ethyl radical $C_2H_5^{\cdot}$ can be assigned to the vibrations of the methyl and methylene groups in ethane and ethylene respectively. It has been noted that the infrared spectrum of this radical shows a number of characteristic features. Thus the low (2842 cm^{-1}) stretching vibration frequency of the β-CH bond, which shields the unpaired electron orbital, is caused[93] by the weak interaction of this bond with the radical centre (Table 6). This is the longest bond in the methyl group.[95] The appreciably lower frequency of the pyramidal deformation vibration of the CH_2 group in the ethyl radical compared with the corresponding vibrations for ethylene is induced by the absence of a π-bond in the ethyl radical and hence by the facilitation of movement of the "pyramidal" type. The broadening of the band due to this vibration is associated with the complex movement (inversion against the background of the internal rotation about the C–C bond) executed by the radical centre. The stretching vibration frequencies of the CH_2 group and the hypsochromic shift of the bands corresponding to the vibrations of the O–C bond in the radical relative to the frequency of the corresponding ethane band indicate a greater strength of all the bonds in the radical fragment; the lengths of these bonds are reduced, which has been confirmed by calculations.[95] Analogous changes have been observed in the methyl radical relative to methane

(Table 5). On the basis of results calculated by the non-empirical SCF LCAO MO method using an extended basis set of Gaussian functions, it has been shown that the formation of the $C_2H_5^+$ cation is accompanied by a further decrease of the length of the C–C bond (Table 6), which apparently entails an increase of its stretching vibration frequency. The carbon atom in the methylene group is sp^2-hybridised, that in the methyl group is sp^3-hybridised, and the HCCH angle is 90°.

Table 6. Parameters of the vibrational spectra and bond lengths of the ethyl radical, the related molecules, and the cation.

Species	Methyl group		Methylene group			ν (C–C), cm^{-1}	r_{CC}, Å	Refs.
	ν (C–H), cm^{-1}	r_{CH}, Å	ν_{sym} (C–H), cm^{-1}	ν_{asym} (C–H), cm^{-1}	δ, cm^{-1}			
H_3C-CH_3	2954	1.102	—	—	—	1016	1.528	[93]
$H_3C-\dot{C}H_2$	2920; 2842	1.076; 1.090	3033	3112	540	1175	1.498	[93]
$H_3C-CH_2^+$	—	—	—	—	—	—	1.48	[91]
$H_2C=CH_2$	—	—	3026; 2989	3106; 3103	949	1623	1.34	[93, 109]

Jackels[96] calculated in terms of the harmonic approximation the vibration frequencies for the methoxy-radical $CH_3O^\cdot$ (Table 7). The values obtained agree well with the experimental data.[97–99]

It has been observed[96] that the C–O bond vibration in the ground state of $CH_3O^\cdot$ has the characteristic value, while in its deuteriated analogue there is a strong interaction of the deformation vibration of the DCO angle with the stretching vibration of the C–O bond. The stretching vibration frequencies of the C–O bond in the excited state, amounting to 678 cm^{-1} for $CH_3O^\cdot$ and 655 cm^{-1} for $CD_3O^\cdot$, have been determined from the fluorescence excitation spectra.[98] In conformity with the results of the calculations[100,101] (Table 7), the formation of the CH_3O^- anion entails an increase of the C–H bond length and the HCO angle and a decrease of the C–O bond length and the HCH angle. The decrease of the C–O bond length is somewhat unexpected, since the formation of an anion from oxygen-containing radicals, for example $NCO^\cdot$, leads to a decrease of the C–O bond vibration frequency, i.e. to an increase of the bond length compared with the radical.

In the methoxide anion the C–O bond length should apparently also increase relative to the $CH_3O^\cdot$ radical, but, since the substituents at the carbon atom are hydrogen atoms, the increase is smaller than for NCO^- and $NCO^\cdot$. Only the deformation vibration of the methyl group, whose frequency has undergone an appreciable bathochromic shift relative to the methyl radical, could be observed for CH_3O^- on the basis of photoelectron spectroscopic data.[102] A quantum-chemical analysis showed[103] that CH_3O^+ has a triplet ground state. On the other hand, according to Bouma et al.,[104] the methoxy-cation is unstable in the singlet state and undergoes the non-activated transition to the hydroxymethyl structure $HOCH_2^+$. In the triplet state the structure of CH_3O^+ is locally stable and has an energy higher by 387 kJ mol^{-1} than that of the singlet $HOCH_2^+$. Thus the formation of the CH_3O^+ cation is associated with the abstraction of an electron occupying a non-bonding orbital in the radical.

Using the second harmonic of a tunable dye laser (310–360 nm), Inoue et al.[105] obtained the excitation and fluorescence spectra of $C_2H_5O^\cdot$. The characteristics of the spectra of the ethoxy-radical are similar to those observed for $CH_3O^\cdot$. Since $C_2H_5O^\cdot$ contains the C–C–O fragment, the similarity of the force constants and the atomic weights of carbon and oxygen leads to the interaction of the C–C–C–O bond vibrations in the ground state. The vibration frequency obtained from the fluorescence spectra, amounting to 1067 cm^{-1}, is therefore associated with the stretching vibration of the C–C–O$^\cdot$ skeleton, in contrast to $CH_3O^\cdot$. According to the results of a non-empirical calculation by the same workers,[105] the 1063 cm^{-1} frequency, which virtually agrees with the experimental value (Table 7), refers to the out-of-phase skeletal stretching vibration of $C_2H_5O^\cdot$ in the ground state, while the 939 cm^{-1} frequency refers to the in-phase vibration. The fact that the frequency of the out-of-phase stretching vibration in $C_2H_5O^\cdot$ is higher than the frequency of the corresponding vibration of $CH_3O^\cdot$ in the ground state agrees with the observed difference between these frequencies for ethyl and methyl alcohols (Table 7). The stretching vibration frequency of the C–O bond in the $C_2H_5O^\cdot$ radical in the excited state is much smaller, as in the case of $CH_3O^\cdot$, than for the ground state. Pinchas[106] gives C–O$^-$ (C–C–O$^-$) bond stretching vibration frequency of the ethoxide anion $C_2H_5O^-$ a value which hardly differs from that of the corresponding vibration in the radical. This agreement may be associated with the fact that the electron which reduces the radical to the anion occupies a non-bonding orbital with the unpaired electron; the anion must then have a singlet electronic ground state.

Table 7. The vibration frequencies and geometrical parameters of the molecules of methanol and ethanol and their derivatives.

Species[a]	ν (CH3), cm^{-1}	r_{CH}, Å	ν(CO), cm^{-1}	r_{CO}, cm^{-1}	δ(CH3), cm^{-1}	α (HCH), °	α (HCO), °	ρ_r, cm^{-1}	Refs.
CH_3O^-	—	1.12	—	1.35; 1.39	1075	102.9	114	—	[100—102]
$CH_3O^\cdot$	3118	1.112	1017	1.405	1330	109.1	111.3	690	[96]
$(CH_3O^\cdot)^*$	—	—	678	—	—	—	—	—	[98]
CH_3OH	2989; 2943; 2835	1.096	1033	1.427	1448	109.2	—	—	[109]
$C_2H_5O^-$	—	—	1068	—	—	—	—	1118	[106]
$C_2H_5O^\cdot$	—	—	1067	—	—	—	—	—	[105]
$(C_2H_5O^\cdot)^*$	—	—	596	—	—	—	—	—	[105]
C_2H_5OH	—	—	1050	—	—	—	—	1095	[106]

[a] The asterisk denotes excited states.

The infrared spectrum of the isopropyl radical in an argon matrix shows[107] four groups of bands (Table 8). The out-of-plane deformation vibration frequency of the radical centre is virtually identical with the value 380 ± 18 cm^{-1} obtained from EPR data.[108] Many observed bands are doublets, which can be accounted for[107] by the existence of more than one conformation of the isopropyl radical. The manifestation of the stretching vibration of the α-CH bond of the radical in the region corresponding to the vibrations of the CH bonds of olefin molecules enabled the authors[107] to conclude that the bond length and the force constant of the radical centre are the same as in olefinic hydrocarbons. This conclusion has been confirmed by the results of a non-empirical SCF LCAO MO calculation. The low frequency of the out-of-plane deformation vibration band of the radical compared with the corresponding vibration of propene[109] shows that the p^2-hybridised carbon atom in the radical consumes less energy on the movement of the "pyramidal" type owing to the absence of the π-bond. We may note that the abstraction of an electron from iso-$C_3H_7^\cdot$ is accompanied by a decrease of the stretching vibration frequency and an

increase of the C–H bond length in the methyl groups (Table 8). The bond lengths in the methyl groups in the pairs $CH_3^{\cdot}$–CH_3^+ and $C_2H_5^{\cdot}$–$C_2H_5^+$ change similarly (Tables 5 and 6). By analogy with the variation of the C–C equilibrium distance (in the C_2H_6–$C_2H_5^{\cdot}$–$C_2H_5^+$ series) (Table 6), one may expect that the C–C bond length in the isopropyl cation is smaller than in the radical which conflicts with the data of Alah et al.[110] It may be that the cause of the 100 cm^{-1} difference between the calculated and experimental asymmetric stretching vibration frequencies of the C–C bond (Table 8) for the cation is the unduly high value of r_{CC} used in the calculation.

Table 8. The vibration frequencies and geometrical parameters of the isopropyl and t-butyl radicals and their cations.

Species	$\nu(\alpha\text{-CH})$, cm^{-1}	ν (C–H) in CH_3, cm^{-1}	r_{CH} in CH_3, Å	δ (CH_3), cm^{-1}	δ_π, cm^{-1}	ν (C–C), cm^{-1}	r_{CC}, Å	α (CCC), °	Refs.
CH_3–$\dot{C}H$–CH_3	3060	2900–2800	1.086–1.090	1500–1390	369	—	1.498	—	[107]
CH_3–$\overset{+}{C}H$–CH_3	—	2730	1.11	1499	—	1260	1.50	—	[110]
CH_3–$\dot{C}H$–CH_3	—	2870–2960	1.085	—	578	920	1.501	—	[109]
$(CH_3)_3C^{\cdot}$	—	2931; 2825	1.084; 1.091	1455; 1370	—	992; 733	1.502	118.4	[111]
$(CH_3)_3C^+$	—	2830	1.11	1455	—	1290	1.500	120	[110]

Notation: $\nu(\alpha\text{-CH})$ is the stretching vibration frequency of the C–H bond which does not shield the unpaired electron orbital in the radical and δ_π represents the out-of-plane deformation vibration.

The infrared spectrum of the t-butyl radical has been interpreted by Pacansky and Chang[111] (Table 8). As for $C_2H_5^{\cdot}$ and iso-$C_3H_7^{\cdot}$, the lengths of the C–H bond in the methyl groups of $(CH_3)_3C^{\cdot}$, which shield the unpaired electron, is greater than the C–H bond lengths in other CH_3 groups. In contrast to the radical, the central $(CH_3)_3C^+$ fragment has a planar structure. The vibrational frequencies of the cation, calculated using the geometrical parameters (Table 8), are virtually identical with the experimental data.

Thus the regularities in the variation of the stretching vibration frequencies and bond lengths for the t-butyl radical and its cation are the same as for the alkyl radicals and their cations presented above: the abstraction of an electron from the radical is accompanied by an increase of the vibration frequency of the bonds (by a decrease of bond lengths) of the fragment losing the unpaired electron and by a decrease of the stretching vibration frequencies (i.e. by an increase of the C–H bond lengths) of the methyl groups.

III. THE VIBRATIONAL SPECTRA OF POLYATOMIC FREE RADICALS AND THE CORRESPONDING IONS

The fluorescence and fluorescence excitation spectra of the cyclohexadienyl radical $C_6H_7^{\cdot}$ (at a concentration of 10^{-3} mole % relative to that of the initial molecules), obtained on irradiation of polycrystalline benzene and deuteriobenzene by fast electrons (energy 9 MeV, dose 10^7 rad) at 77 K, have been investigated[112] at 4.2 K. The source of excitation of the fluorescence was a UV-1000 nitrogen laser. Treating the radical as a benzene "molecule", the authors assigned the fluorescence lines at 5586 and 5516.5 Å to the 0–0 transition in $C_6H_7^{\cdot}$ and $C_6D_7^{\cdot}$ respectively. The shift of the absorption lines for the deuteriated specimen was 139 cm^{-1}. The vibrational frequencies of the ground and excited states of $C_6H_7^{\cdot}$ and $C_6D_7^{\cdot}$ are close to those of the corresponding benzene vibrations. On the basis of the frequency shift on deuteriation, the authors assigned the 552, 1169, and 1566 cm^{-1} bands in the spectrum of the cyclohexadienyl radical to the ν_6, ν_9, and ν_8 (C_{2g}) vibrations (Wilson's numbering).

Perkampus[113] investigated the infrared spectra of deposited films of salts having the composition ArH–HX–MX_3 (where ArH = benzene or methylbenzene and MX_3 = $AlCl_3$, $AlBr_3$, $GaCl_3$, or $GaBr_3$) at low temperatures. The nature of MX_3 does not exert a significant influence on the spectrum of the complex. The observed spectra differ appreciably from those of the aromatic hydrocarbons ArH and have been attributed to the carbonium salts $ArH_2^+MX_4^-$. The absorption bands of the anions AlX_4^- and $Al_2X_7^-$ have been detected in the infrared spectra of the complexes,[114] which serves as additional evidence for the ionic structure of the complexes: $ArH_2^+AlX_4^-$ and $ArH_2^+Al_2X_7^-$. The addition of a proton to ArH alters the symmetry of the aromatic ring (from D_{6h} for benzene to C_{2v} for the complex), as a result of which some of the bands, which are forbidden for the initial hydrocarbon, appear in the spectrum of the adduct. For example, the 1595 cm^{-1} band, observed in the spectra of substituted benzene derivatives, has been interpreted as due to the skeletal vibration of the C=C bond. On the basis of these considerations and taking into account the influence of the substitution of hydrogen by deuterium on the spectra, the vibration frequencies of the $C_6H_7^+$ ion were assigned[113] (Table 9). The new band at 640 cm^{-1}, observed in the spectrum of the benzene complex, corresponds to the 490 cm^{-1} band in the spectrum of its deuterio-analogue. The relatively large isotope shift enabled the authors to assign this band to a vibration of the C–H bond.

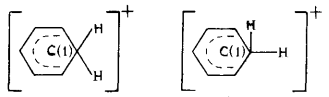
Table 9. Assignment of the bands in the infrared spectrum of $C_6H_7^+$.

Vibration (after Wilson)	Symmetry	ν, cm^{-1}		Vibration mode	ν, cm^{-1}
		C_6H_6	$C_6H_7^+$ [113]		$C_6H_7^+$ [112]
$\nu_{8a,\ b}$	E_g^+	1596	1595 s.; 1580 v.w.	β(CCH), Q(CC)	1566
ν_{19}	E_u^-	1485	1445 v.s.	β(CCH), Q(CC)	—
ν_3	A_{2g}	1326	1328 v.w.	β(CCH)	—
ν_9	E_g^+	1178	1205 m.	β(CCH), Q(CC)	1169
ν_{15}	B_{2u}	1146	1178 s.	β(CCH), Q(CC)	—
ν_5	B_{2g}	985	983 v.w.	ρ(C–H), $\varkappa$(CCC)	—
ν_{17}	E_u^-	970	953 w.	ρ(C–H), $\varkappa$(CCC)	—
ν_1	A_{1g}	992	901 m.; 814 m.	Q(CC)	—
ν_{11}	A_{2u}	671	690 v.s. 640 v.s.	ρ(C–H)	—
ν_6	E_g^+	606	881 w.	γ(CCC)	552

Notation: s. = intense (strong) absorption band, v.w. = very weak band, v.s. = very intense band, w. = weak band, and m. = moderately intense band.
Note. The numerals in square brackets denote references (Ed.of Translation).

A similar study has also been carried out for methylbenzenes.[115] The spectra were interpreted on the assumption that σ-complexes are formed in which the proton adds to one of the carbon atoms of the aromatic ring via a σ-bond

produced by two electrons from the aromatic sextet localised in a hybrid sp^3 orbital of the carbon atom. In the limiting case both hydrogen atoms at C(1) are equivalent and are disposed symmetrically relative to the plane of the ring [structure (I)]:



(I) (II)

However, Bystrov[116] drew attention to the great similarity between the spectra of the σ-complex of benzene and monosubstituted benzenes; this enabled him to postulate that the π-electron system of benzene in the σ-complex is perturbed to a much lesser extent than is represented in structure (I) and that the benzene carbonium ion has the structure (II), in which the added proton is held by a σ-bond, formed by the electrons located in the *p*-orbital of the carbon atom. Such a structure can then be regarded as a "localised" π-complex differing from the usual π-complexes in which identical interactions of the proton with all the π-electrons of the aromatic sextet are assumed.

In the infrared spectra of complexes of methylbenzenes with $AlBr_3$ and HBr, an intense band has been observed[117] in the vicinity of 2800 cm^{-1}, the band being absent from the spectrum of the complex of hexamethylbenzene; it was assigned to the stretching vibrations of the CH_2 group. The absorption band corresponding to this group is broadened and displaced towards lower frequencies on passing from the anthracene complex to mesitylene, toluene, and benzene complexes, i.e. with decrease in the basicity of the hydrocarbon involved in the formation of the complex.[118] The integral intensity of the absorption bands of the quasi-aliphatic CH_2 groups of the arenium ions increases consistently with increase in their proton-donating capacity (with decrease of the basicity of the hydrocarbon). The less basic the hydrocarbon, the more marked the "acid" character of the hydrogen atoms of the quasi-aliphatic CH_2 group of the arenium ion and the greater its tendency towards involvement in the formation of hydrogen bonds. This leads to a broadening of the absorption band of the CH_2 group, to an increase in its intensity, and to its hypsochromic shift. The authors[118] regard the results as experimental confirmation of the hyperconjugation of the C–H bonds of the quasi-aliphatic CH_2 group with the positively charged carbon atoms of the pentadienyl component of the arenium ions.

This conclusion agrees with the results of a study of the Raman spectra of the mesitylene ion,[119] for which a single absorption band of moderate intensity has been observed in the range 1500–1600 cm^{-1} at 1625 cm^{-1} with a depolarisation coefficient $\rho = 0.65$. A single band of moderate intensity has also been observed in the Raman spectra of mesitylene at 1610 cm^{-1} with $\rho = 0.72$. In the spectra of unsaturated cyclic compounds containing conjugated carbon–carbon bonds of the non-aromatic type,[119] two lines are usually observed, one of which (corresponding to a symmetrical stretch) is very intense and polarised ($\rho = 0.1$–0.2). For aromatic compounds of the benzene series, the corresponding lines are depolarised ($\rho = 0.7$–0.8).[119] The position, degree of depolarisation, and relative intensity of the line of the mesitylene ion are evidence that the formation of the CH_2 group on protonation of mesitylene does not induce a complete overlap of the conjugation in the ring. This is possible only in the presence of an intense hyperconjugation of the C–H bonds in the CH_2 group with the pentadienyl component of the ion. The hypsochromic shift of certain vibration frequencies in the spectrum of the arenium cation $C_6H_7^+$ [113] (Table 9) relative to the frequencies of the analogous vibrations of the $C_6H_7^{\cdot}$ radical[112] must be attributed to an increase in the corresponding force constants.

Pellois et al.[120] investigated the quasi-line fluorescence spectrum of the triphenylmethyl radical $Ph_3C^{\cdot}$ obtained as a result of the photodissociation of triphenylmethane at 9 K in a methylcyclopentane matrix. The spectrum is due to the 0–0 transition and consists of ~50 bands in the region of 19 400 cm^{-1}. The spectrum was interpreted on the assumption that the triphenylmethyl radical should be assigned to the D_3 symmetry point group (on the basis of the data obtained with the aid of electron diffraction).

Weston et al.[121] investigated the infrared spectra and assigned the vibration frequencies of the triphenylmethyl cation $Ph_3C^+_{(1)}$ and its isotope-substituted analogues (with 1-^{13}C and Ph-d_5). It was concluded that the cation belongs to the D_3 symmetry point group, in agreement with the X-ray diffraction data, according to which the three central C–C bonds lie in a single plane. The length of each is 1.45 ± 0.018 Å, which is much less than the length of a single C–C bond (1.54 Å). The aromatic rings are slightly non-planar and are displaced from the plane of the C–C bonds by 32° in a propellar fashion. The lengths of the C–C bond within the limits of the rings [1.41, 1.36, and 1.37 Å for C(1)–C(2), C(2)–C(3), and C(3)–C(4) respectively] differ somewhat from that in benzene (1.40 Å). Comparison of the frequencies in the spectra of the triphenylmethyl radical and the triphenylmethyl cation indicates an appreciable increase of the Ph–C vibration frequency (from 1300 cm^{-1} for the radical to 1395 cm^{-1} for the cation), in agreement with the decrease of the Ph–C bond length in the case of the cation. The increase in out-of-plane deformation vibration frequencies of the C–H bonds in the ring corresponds to a decrease of the π-electronic charges on the carbon atoms. The decrease (by 15 cm^{-1}) of the stretching vibration frequency of the bonds in the ring and the increase (by 15 cm^{-1}) of the in-plane C–H deformation vibration frequencies are apparently caused by a change in the force constants of the ring bonds as a consequence of the change in their lengths.

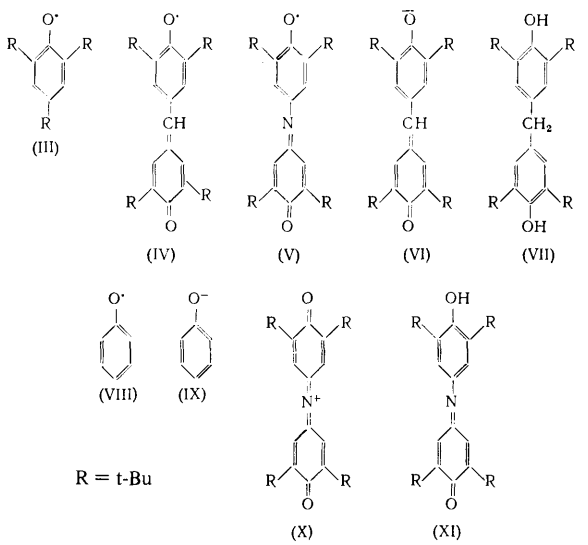
Meda et al.[122] investigated the resonance Raman spectra of the triphenylmethyl cation and anion on excitation by an argon laser. Their vibration frequencies differ very little, since the two electrons of the anions are located in a non-bonding molecular orbital. Appreciable differences are observed between the intensities and particularly between the degrees of depolarisation of the principal polarised bands. It has been suggested that the cation has the D_3 symmetry (planar propeller), while the anion has the C_3 symmetry (dome-shaped propeller).

The infrared spectrum of the allyl radical[123] consists of 16 bands; the observed frequencies agree in broad outline with the spectrum predicted for the allyl ligand (C_S symmetry) on the basis of data for π-allyl organometallic compounds.[124] However, the number and positions of the bands of the allyl radical in the range 500–1000 cm^{-1} correspond to a higher symmetry (C_{2v}) of this species, for which there are two A_2 type vibrations which are inactive in the infrared spectrum.

Saurissean et al.[125] compared the vibrational characteristics and the structures of the allyl radical $C_3H_5^{\cdot}$ and the allyl anion $C_3H_5^-$ involved in π- and anionic bonds with metals. The bands due to the skeletal stretching vibrations at 1383 and 1023 cm^{-1} in the infrared spectra of the π-allyl complexes have been interpreted as due to the asymmetric [ν_{asym}(CCC)] and symmetrical [ν_{sym}(CCC)] vibrations. The bands at 1491 and 1232 cm^{-1} have been assigned to the same vibrations on the basis of a theoretical analysis of the molecular vibrations.[124] In the case of ionic compounds, the bands at 1527 and 1022 cm^{-1} correspond to the ν_{asym}(CCC) and

ν_{sym}(CCC) vibrations. Calculations have shown that, on passing from $C_3H_5^{\cdot}$ to $C_3H_5^-$, there is a small increase of the force constants K_{C-C} and also an increase of the CCC angle from 120° to 140°. The observed decrease of the frequencies of the in-plane deformation vibrations of the CH_2 and CH groups (from 5 to 8%) reflects the change in the corresponding force constants. The intensities of the in-plane vibration bands of the CH_2 group increase on passing from the π-complexes to the ions, while the opposite behaviour has been observed for the out-of-plane deformation vibrations of the same groups. This indicates a strong anisotropic perturbation of the π orbitals in $C_3H_5^-$. The half-widths of the majority of the intense bands in the spectra of ionic compounds are much greater in the spectra of the π-complexes.[125] Thus the band half-width for the vibrations of the CH_2 group changes from 10 to 50 cm^{-1} and that for δ(CCC) changes from 15 to 75 cm^{-1}. This change is caused by the greater localisation of the electrons at the CH_2 groups in the anion as compared with the radical. The vibration frequencies of the C–H bonds in the π-complexes, which are in the range above 3000 cm^{-1}, are consistent with the aromatic character of these bonds. The ν(C–H) frequencies for the ions are observed at 2990 cm^{-1}.

The infrared spectra of the sterically hindered phenoxy-radicals (III)–(V) have been studied systematically.[126,127] The Raman spectrum of the radical (IV) has also been investigated;[128] the frequency assignment is identical with that carried out by Samoilenko and Kotorlenko.[127]

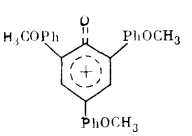


The spontaneous Raman spectra of the phenoxy-radical $C_6H_5O^{\cdot}$ [129] have five polarised bands in the frequency range below 1700 cm^{-1}: at 1615, 1596, 1485, 1382, and 1202 cm^{-1}. The first has been assigned to the vibrations of the C–O$^{\cdot}$ bond, which agrees with other data.[126] The results of Shindo and Hiraishi[129] confirm the conclusion that there is a significant difference between the vibration frequencies of the phenoxy-radical and the corresponding phenol, which had been reached earlier[126,127] on the basis of the change in the force field parameters and not the mode of the vibrations.

The intense band at 1613 cm^{-1} in the resonance Raman spectrum of the radical (IV) has been attributed[130] to the stretching vibration on the C–O$^{\cdot}$ bond, in agreement with the earlier assignment.[127,128] The intense Raman band at 1585 cm^{-1} and the weak band at 1560 cm^{-1} were assigned[130] to the ν_{8a} and ν_{8b} vibrations respectively, while the weak bands at 1540 and 1528 cm^{-1} were assigned to the ν_{19a} and ν_{19b} vibrations.

It is impossible to agree fully with this interpretation, because, owing to the presence in the radical of two equivalent rings, each vibration is split into two. Taking into account the results of the calculation of the vibration spectrum of the radical (IV),[127] the two bands at 1585 and 1560 cm^{-1} must be attributed to the ν_{8a} vibration, which is split into A_1 and $B_1(C_2)$, while the bands at 1540 and 1528 cm^{-1} must be assigned to the ν_{19b} vibration also split into A_1 and B_1 respectively. The band at 1336 cm^{-1} should apparently be assigned to the symmetrical vibration of the bridge and that at 1292 cm^{-1} to the ν_{19a} vibration. The bands at 1226 and 1212 cm^{-1} can be interpreted as due to the ν_{18a} and ν_{18b} vibrations. This interpretation corresponds to the calculated frequencies[127] and agrees with experimental data. For the excited state, the C–O$^{\cdot}$ vibration frequency falls to 1543 cm^{-1} as a result of the interaction with the system of π-bonds. It has been concluded that the resonance Raman spectra can be recorded at concentrations of this radical less than 10^{-7} M, which makes this method promising for the investigation of radical reactions in experiments involving pulse radiolysis.

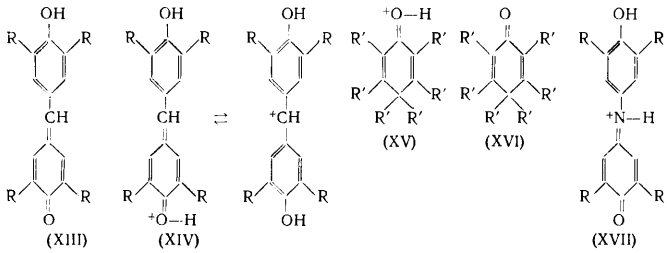
On the basis of infrared, Raman, and electronic absorption spectra, Aleksandrova and Kotorlenko[128] concluded that the rings of the anion (VI) are equivalent, as a consequence of which its symmetry (C_2) is analogous to the local symmetry of the molecule of the phenol (VII) and the radical (IV). Comparison of the vibrational spectra of the anion (VI) with those of the phenol (VII) and the radical (IV) led the authors[128] to the conclusion that the vibration frequencies of the anion have intermediate values between those of the phenol and the radical and that they are closer to the frequencies of the phenol. The hypsochromic shift of the vibration band of the C–O$^-$ bond in the phenoxide anion (VI) relative to the phenol (VII) (by 40 cm^{-1}; Table 10) is close to that obtained[131] for the unsubstituted anion (VIII) and the corresponding phenol (IX) (25 cm^{-1}). The calculated change in the force constant of the C–O$^-$ bond of the anion (VI) compared with the constant for the phenol (VII) is 0.36×10^{-6} cm^{-2}, while for the radical (IV) it amounts to 6.88×10^{-6} cm^{-2}. The slight increase of the vibration frequency of the C–O$^-$ bond and of the force constant K_{C-O} in the spectrum of the anion (VI) compared with the phenol (VII) enabled the authors to assume that the negative charge of the anion is localised predominantly on the two oxygen atoms and that this is responsible for the similarity of the spectra of the anion (VI) and the phenol (VII). The intense band at 1625 cm^{-1} was assigned to the C–O bond of the cation (X),[132] because, according to quantum-chemical calculations, it should be located between ν(C–O$^{\cdot}$) for the radical (V) (1586 cm^{-1}) and ν(C=O) for the indophenol (XI) (1642 cm^{-1}). The assignment agrees with the presence in the infrared spectrum of the cation (XII) of the ν(C...O) band at 1613 cm^{-1},[133] and is confirmed by the presence in the infrared spectrum of the cation (X) of a band at 1865 cm^{-1}, which has been interpreted[132] as being due to the asymmetric stretching vibration of the conjugated bond system C=N=C.



(XII)

The bathochromic shift of this band relative to the band of the ion NO_2^+ (2360 cm^{-1}) can be explained by the greater shift of the electron density to N^+ from the C=N bonds than from the N=O bonds. The increase of the force constant of the C=O bond in the cation (X) compared with that of the

radical (V) is 0.78×10^{-6} cm^{-2}. The formation of the cation (XIV) in the interaction of the phenol (XIII) with acids has been demonstrated.



(XIII) (XIV) (XV) (XVI) (XVII)

R = t-Bu, R′ = Me

The similarity of the infrared spectrum of the latter cation to that of the anion (VI) as regards the number and positions of the bands enabled the authors[132] to conclude that these molecules belong to the same symmetry group (C_2). This means that the cation (XIV) has two equivalent rings and two OH groups, which has been confirmed by ^{1}H NMR spectra.

The absorption by the hydroxy-group is observed in the infrared spectrum of the cation (XIV) in the region of 3570 cm^{-1}. The high frequency of this band is consistent with the ^{1}H NMR data, indicating the localisation of the positive charge predominantly on the carbon atom of the bridging CH group. The intense band at 1203 cm^{-1} has been assigned to the vibration of the C–O bond. The shift of the band by 45 cm^{-1} compared with the corresponding band of the phenol (XIII) (1158 cm^{-1}) was explained by the author by the redistribution of electron density. The increase of the force constant of the C–O bond in the cation (XIV) relative to compound (XIII) owing to the increase of the amount of double bond character was 0.64×10^{-6} cm^{-2}.

The formation of the hydroxyhexamethylbenzenium cation (XV) on interaction of hexamethyldienone (XVI) with $AlCl_3$ and HCl in CH_2Cl_2 has been investigated.[134] The broad band at 3450 cm^{-1} has been assigned to the stretching vibration of the OH group involved in the hydrogen bond. The 1510 cm^{-1} band was assigned to the stretching vibration of the C–O bond and the band at 1630 cm^{-1} was assigned to the vibrations of the C–C bonds of the ring with an order of 1.5. It is noteworthy that the shift of the positive charge to the bridging carbon atom induces a rearrangement of the quinonoid ring into an aromatic form, while in the cation (XV) the quinonoid structure is largely retained.

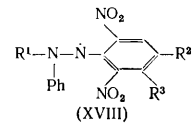
Bands referring to the vibrations of the phenyl and quinone imine rings have been observed[132] in the infrared spectrum of the cation (XVII) obtained by the protonation of the phenol (XI) at the nitrogen atom. A bathochromic shift of the vibration band of the O–H bond at 3615 cm^{-1} relative to the spectrum of compound (XI) (3627 cm^{-1}) has been observed. The broad band at 3515 cm^{-1} was assigned to the $\overset{+}{N}$–H vibration, while the bands at 1640 and 1660 cm^{-1} were assigned respectively to the vibrations of the C=C and C=O bonds of the quinone imine ring. The bathochromic shift of the O–H and N–H bond vibrations relative to the neutral molecules led to the conclusion that the $\overset{+}{N}$–H bond is stronger than the $\overset{+}{O}$–H bond, which was confirmed by chemical experiments. Since the analysis of the vibration modes of phenol, the radical, and the quinonoid structures[126,127] indicates the predominant contribution of the same coordinate to the vibrations in question, the observed frequency shifts and the changes in the force constants permit inferences about the changes in the structures of the compounds in the series under consideration (Table 10).

It follows from the analysis of the data in Table 10 that the addition of a proton to the carbonyl group of the phenol and of an electron to the radical diminishes while the abstraction of an electron and the addition of a proton to the nitrogen atom of the bridging group increases the contribution of quinonoid structures.

Table 10. The vibration frequencies and force constants of the bonds in phenols and the corresponding radicals and ions.

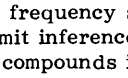
Species	ν (C–O), cm^{-1}	ν (CO), cm^{-1}	ν (C=O), cm^{-1}	$10^6 K_{C-O}$, cm^{-2}	$10^6 K_{CO}$, cm^{-2}	$10^6 K_{C=O}$, cm^{-2}	Refs.
(IX)	1256	—	—	—	—	—	[131]
(VIII)	1281	—	—	—	—	—	[131]
(XV)	—	1510	—	—	—	—	[134]
(III)	—	1573	—	—	—	—	[132]
(XVI)	—	—	1635	—	—	—	[134]
(XIII)	1158	—	1615	7.00	—	14.90	[132]
(VI)	1195	—	—	7.36	—	—	[128]
(XIV)	1203	—	—	7.64	—	—	[132]
(IV)	—	1583	—	—	13.88	—	[127]
(XI)	1156	—	1642	—	—	—	[127]
(XVII)	1203	—	1660	—	—	—	[132]
(V)	—	1586	—	—	—	—	[137]
(X)	—	—	1625	—	—	—	[132]

The infrared spectra of a series of free radicals of the hydrazine type (XVIII) have been investigated:[135,136]



(XVIII)

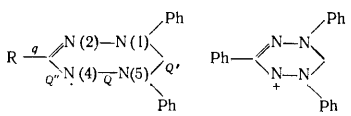
It has been noted that the intense doublet in the spectrum of the radical (XVIII) (bands at 1620 and 1600 cm^{-1}), assigned to the skeletal vibrations of the picryl and monosubstituted rings respectively, has undergone a bathochromic shift by ~20 cm^{-1} compared with the initial molecule, which is due to the increased conjugation owing to the appearance of an unpaired electron at the β-nitrogen atom. The moderately intense band in the range 1210–1250 cm^{-1} has been assigned to the stretching vibrations of the central N–N fragment. On excitation of the diphenylpicrylhydrazyl radical (DPPH) in benzene by means of a pulsed tunable dye laser (λ = 4880 Å), Wilbrandt et al.[137] observed an increase of the intensity of this band in the resonance Raman spectrum.

The spontaneous Raman spectra of the DPPH radical and of the initial diphenylpicrylhydrazine were obtained in a later study.[138] It was noted that, on passing to the radical, the analogous bands undergo a bathochromic shift, because the unpaired electron occupies as a rule antibonding molecular orbitals. New bands at 1205 and 1292 cm^{-1}, having moderate and low intensities respectively, have been observed in the spectrum of the DPPH radical. The authors[138] suggest that the bands at 1280 and 1290 cm^{-1} in the spectra of the molecule and the radical can be analogues, but noted that the increase of the frequency of this vibration on passing from the hydrazine molecule to the radical is then obscure and requires interpretation. The authors[138] proposed such an interpretation of the bands on the grounds that the vibrations of the  group in both species are quasi-characteristic. In the hydrazine molecules this

chain should be bent and a single intense fully symmetrical vibration should appear accordingly in the spontaneous Raman spectrum. In solutions of the DPPH radical the above chain straightens out, which is accompanied by a change in the hybridisation of the bonding orbitals of the N atom from sp^2 to sp. This leads to additional and significant asymmetry owing to the delocalisation of the unpaired electron. In conformity with selection rules, two fully symmetrical stretching vibrations now become active in the spontaneous Raman spectrum, to which the authors[138] assigned new bands at 1205 and 1292 cm^{-1}. Both these vibrations should be intense also in the infrared spectrum, which has indeed been observed.[136] The observed change in the geometry of the species rules out the possibility of comparing the N–N bond vibrations in the diphenylpicrylhydrazine–DPPH radical pair in solutions. According to the above data,[138] when the DPPH radical passes to a crystalline state, the hybridisation of the orbitals of the nitrogen atom again changes from *sp* (for the solution) to sp^2 and coincides with that for the initial molecule.

Mielke and Ratajczak[139] carried out a calculation for the normal vibrations of the molecule of hydrazine and its protonated derivatives $N_2H_5^+$ and $N_2H_6^{2+}$ in terms of a modified valence force field approximation. It was found that the diagonal force coefficients, ν(N–N), and δ(HNH) decrease monotonically on passing from N_2H_4 to $N_2H_6^{2+}$. The observed distribution of the potential energy indicates the absence of a significant change in the vibration modes for $N_2H_6^{2+}$. This finding suggests that the decrease of the force constant for the N–N bond on passing from hydrazine to protonated hydrazine is due to the decrease of the degree of delocalisation of the unshared electron pair from the nitrogen atoms to the N–N bond.

Studies of the infrared spectra of stable verdazyl radicals (XIX) have been considered in reviews:[1,140]



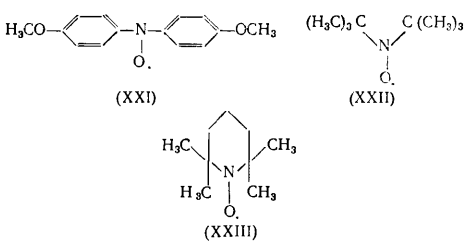
(XIX) (XX)

R = Ph (TPV), H

However, the assignment of the frequencies to the vibrations of individual bonds was not rigorous, since the similarity of the atomic weights of nitrogen and carbon entails an intense interaction and the normal vibrations of the heterocycle must have complex modes. For a reliable interpretation of the spectrum of the triphenylverdazyl radical (TPV) (XIX), a calculation has been made[141] of the frequencies and modes of the vibrations for two conformations—chair and boat. The correctness of the force field parameters obtained has been confirmed by the satisfactory agreement between the calculated and experimental changes in the vibration frequencies of the heterocycle with the ^{15}N atoms in the 2- and 4-positions. The calculation showed that the vibrations of the heterocycle of the TPV radical are described by complex modes. The interpretation of the complex band at 1330 cm^{-1} was revised and it was shown that it consists of two bands, the more intense of which (at 1330 cm^{-1}) is caused mainly by the deformation of the angles β(NCH), while the band at 1315 cm^{-1} is due to the vibrations of the N–Ph bonds. In addition the bands at 1400 cm^{-1} [Q''(CN), Q'(C–N)] and at 1380 cm^{-1} [q(C–C), Q(N–N), Q''(CN)] were assigned to the vibrations of the heterocycle.

The change in the infrared spectra on one-electron oxidation of the TPV radical to the corresponding cation (XX) has been investigated.[141,143] In order to obtain a quantitative characteristic of the change in the electronic structure following the abstraction of an electron from the TPV radical, the vibrational spectrum of the cation (XX) having the boat conformation was carried out. The geometrical structure of this cation was found quantum-chemically by minimising the total energy of the corresponding system with respect to the nuclear coordinates; it was shown that it differs insignificantly from the geometrical structure of the TPV radical. The experimental[141] band shift on passing from the TPV radical to the cation (XX) made it possible to find the changes in the bond force constants and the interaction constants. The increase of the force constant K_Q corresponds to a shift of electron density from the nitrogen atoms in the 1- and 5-positions to the N–N bonds, which agrees with the abstraction of an electron from the nitrogen atoms in the 2- and 4-positions on oxidation of the TPV radical to the cation (XX), which has been established on the basis of quantum-chemical calculations and X-ray electronic spectra.[144] The decrease of the force constants K_Q and K_q indicates an increase of the positive charge on the N(1) and N(5) atoms, while the decrease of the interaction constants $H_{QQ''}$, $H_{Q''Q''}$, and H_{Qq} agrees with the decrease of the degree of delocalisation of the unshared electron pair from the N(1) and N(5) atoms to the benzene rings, as a consequence of which the frequency of the out-of-plane deformation vibrations of the hydrogen atoms in the benzene rings increases and the intensity of their stretching vibrations diminishes.

The band at 1345 cm^{-1} in the spectrum of the dimethoxydiphenylnitroxy-radical (XXI) has been assigned to the vibration of the N–O· bond.[135] Comparison of the infrared spectra of the di-t-butylnitroxy-radical (XXII) [145] and the 2,2',6,6'-tetramethylpiperidin-1-yloxy-radical (XXIII) [146] with the infrared spectra of the corresponding amines established that the N–O· band is also at 1345 cm^{-1}.

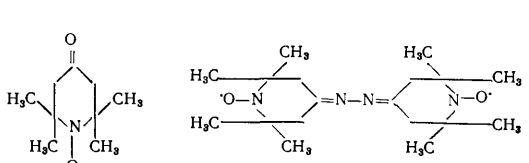


(XXI) (XXII)

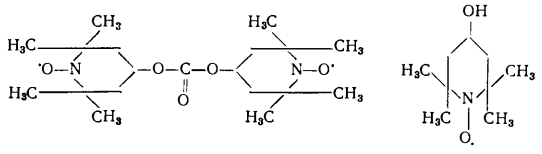
(XXIII)

The similarity of the atomic weights of carbon, nitrogen, and oxygen raises the question of the extent to which the vibrations of the N–O· bond are characteristic. A study has been made[147] of the infrared spectra of the radicals (XXII) and (XXIII) and also the frequencies and modes of their normal vibrations were calculated, which served as a basis for the interpretation of their vibration spectra, a model was proposed for the force field, and it was shown that the vibrations of the N–O· bond are characteristic as regards frequency, mode, and intensity.

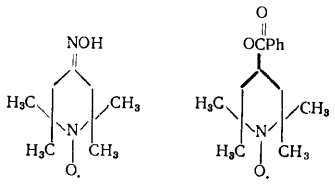
It has been shown with the aid of the ^{15}N label[148] that the N–O· band in the infrared spectra of other radicals of the piperidine series is at 1380 cm^{-1} [the radicals (XXIV) and (XXV), 1367 cm^{-1} [the radical (XXVI)], and 1371 and 1342 cm^{-1} [the radical (XXVII)].



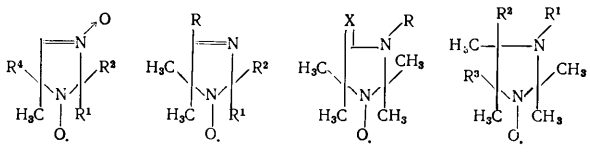
(XXIV) (XXV)



(XXVI) (XXVII)



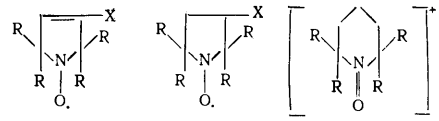
(XXVIII) (XXIX)



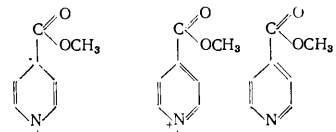
(XXX) (XXXI) (XXXII) (XXXIII)

Intense bands, assigned to the vibration of the N–O bond, have been observed in the Raman spectra of the radicals (XXIV) and (XXVII) [149]—at 1370 cm^{-1} for (XXIV), at 1370 and 1359 cm^{-1} for (XXVII), and at 1362 and 1352 cm^{-1} for the radicals (XXVIII) and (XXIX) respectively. The higher N–O$^{\cdot}$ bond vibration frequency for the radical (XXIV) compared with (XXIII) can be accounted for by a difference in its steric structure. While the radical (XXIII) has the chair conformation,[150] the radical (XXIV) has the twisted boat conformation with an angle of twist at 28°.[151] The increased order of the exocyclic bond in the 4-position promotes the delocalisation of electrons in the ring,[152] which is accompanied by an increased amount of double bond character of the N–O$^{\cdot}$ bond and an increase in the corresponding frequency. The presence of two bands in the spectrum of the radical (XXVII) is apparently caused by both intramolecular and intermolecular hydrogen bonds. In dilute solutions this radical has the boat conformation with an intramolecular hydrogen bond,[151] whereas in the crystalline state the molecules are linked by hydrogen bonds into infinite chains and have a distorted chair conformation.[151] The similarity of the N–O$^{\cdot}$ bond vibration frequencies in the spectra of the radicals (XIX) and (XXIII) agrees with the conclusion of Kotorlenko et al.[147] that there is no shift of the N–O$^{\cdot}$ bond vibration frequency when the hydrogen is replaced by carbon at the C(3) atom of the radical (XXIII) and also that the vibration mode remains unaltered.

The N–O$^{\cdot}$ bond vibration frequencies for radicals of the imidazoline [the radicals (XXX) and (XXXI)] and imidazolidine [the radicals (XXXII) and (XXXIII)] series have been interpreted on the basis of their Raman spectra and also by measuring the isotope shift after the introduction of ^{15}N in the 1-position in the imidazoline ring. It has been established that the vibration band of the N–O$^{\cdot}$ bond in the infrared and Raman spectra of these radicals is at 1438 ± 5 cm^{-1} and the observed isotope shift (27 cm^{-1}) agrees with the calculated value (28 cm^{-1}). Calculation of the frequencies and modes of the normal vibrations of these radicals[149] showed that the vibration of the nitroxy-group is characteristic in terms of the frequency. The N–O$^{\cdot}$ bond vibration bands of five-membered nitroxy-radicals of the pyrroline [the radical (XXXIV)] and pyrrolidine [the radical (XXXV)] series are located in the same part of the spectrum. It has been concluded[149] that the position of the N–O$^{\cdot}$ band in the spectra of cyclic nitroxy-radicals depends on the ring size.



(XXXIV) (XXXV) (XXXVI)



(XXXVII) R=CH_3 (XXXVIII) (XXXIX)

The vibrational spectra of nitroxy-radicals and biradicals in the region of the stretching vibrations of unsaturated carbon–carbon bonds and the stretching vibrations of the CH and OH groups have been investigated by Bovina et al.[153]

The conversion of the nitroxy-radical (XXIII) into the corresponding cation (XXXVI) is accompanied by a change in the N–O$^{\cdot}$ bond vibration frequency from 1345 cm^{-1} for the radical to 1630 cm^{-1} for the cation, which is caused by the decrease of the length of this bond from 1.30 Å [154] to 1.19 Å [152] respectively and in addition by the change from the chair conformation (XXIII) [150] to the twisted boat conformation (XXXVI) with an angle of twist of 24°30′.[152] The decreased length and the strengthening of the N–O$^{\cdot}$ bond following the one-electron oxidation of the radical (XXIII) has been explained[152] by the fact that the unpaired electron in nitroxy-radicals is located in an antibonding orbital and that the conversion of these radicals into cations entails the loss of this electron. In our view, the oxidation of the radical (XXIII) to the cation (XXXVI) is accompanied by the abstraction of an electron from the unshared electron pair of the nitrogen atom with subsequent pairing of the two unpaired electrons located in the O and N atoms.

Kosover and Poziomek[155] quote the C=O bond vibration frequencies for 1-ethyl-4-methoxycarbonylpyridinium iodide (XXXVIII) (1730 cm^{-1}), 1-ethyl-4-methoxycarbonylpyridinyl (1642 cm^{-1}) (XXXVII), and methyl isonicotinate (XXXIX) (1736 cm^{-1}), which increase the decreased degree of displacement of the electron density to the ring. On the other hand, the ring stretching vibration frequencies diminish on passing from the pyridinyl radical (XXXVII) [156] to protonated pyridine[157] and further to pyridine (XXXIX).[109]

Thus the abstraction of an electron from neutral polyatomic free radicals is accompanied, as in the case of the simple radicals, by an increase of the vibration frequency and strength of the bond adjoining the atom from which the electron is abstracted, while the addition of an electron entails a decrease in the vibration frequency and order of the bond.

Comparative analysis of the vibrational spectra of neutral free radicals and the corresponding ions—the products of the one-electron reduction or oxidation of these radicals—makes it possible to infer the changes in both the geometrical and electronic structures of the species and to predict the sites of increased reactivity.

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Pisarzhevskii Institute of
Physical Chemistry,
Academy of Sciences of
the Ukrainian SSR, Kiev

Translated from *Uspekhi Khimii*, 54, 1985-2008 (1984) U.D.C. 541.579.547

The Hydrogen Bond and CH Acidity

V.K.Pogorelyi and T.B.Vishnyakova

A systematic account is given of quantitative data on the properties of the hydrogen bonds formed by CH acids as proton donors and the influence of the nature of the substituents and of the steric and electronic structures of CH acids on the strength of these bonds is discussed. The studies in recent years devoted to the equilibrium and kinetic CH acidity are examined and the factors responsible for what is in many instances an "anomalous" behaviour of CH acids are analysed. The proton-donating capacity in hydrogen bonds and CH acidity are compared.
The bibliography includes 108 references.

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I. INTRODUCTION

Protolytic reactions occupy one of the central positions in the chemistry of organic compounds. CH acids, grouped in a special class of compounds, have been arousing constant interest owing to the specific features of the factors determining their reactivity.[1,2] Hydrogen bonds involving CH acids[3] play an important role in protolytic reactions, since their properties influence the kinetics and mechanism of reactions involving proton transfer. The quantitative results of studies in this field are so far not numerous, but it is already clear that even relatively weak C–H...B hydrogen bonds can alter not only the energy profile of the process but also its probability characteristics, because the reactants involved in hydrogen-bonded complexes are close to one another and are oriented relative to the proton transfer reaction coordinate.

The question of the relation between the proton-donating capacity in C–H...B hydrogen bonds and thermodynamic and kinetic CH acidity arises naturally. For OH, SH, and NH acids, these relations have been studied on numerous examples.[4,5] On the other hand, in the case of CH acids, such comparisons have seldom been made. This review deals with the quantitative results of studies of hydrogen bonds and the acidity of CH groups polarised by electron-accepting substituents. The characteristics of the influence of the steric and electronic structures of CH acids on the strength of C–H...B hydrogen bonds are analysed. In conclusion, the proton-donating capacity of CH acids is compared with their kinetic and equilibrium acidities.

II. ASSOCIATION OF HALOGEN-SUBSTITUTED HYDROCARBONS

The CH groups polarised by electronegative halogen atoms form C–H...B hydrogen bonds with various bases. One of the first compounds for which such bonds had been observed spectroscopically was chloroform.[6] After the addition of bases, B, to chloroform, an increase of the width and intensity of the stretching vibration band is observed in its infrared spectrum, while for strong bases this band undergoes a bathochromic shift.[3] For example, in mixtures with triethylamine (TEA) the magnitude of this shift $\Delta\nu$(CH) reaches 80 cm^{-1}.[6]

Table 1. Thermodynamic characteristics of the association of $CHCl_3$ with various electron donors in cyclohexane and carbon tetrachloride.[7,13,19]

Electron donor	$-\Delta H$, kcal $mole^{-1}$	$-\Delta S$, e.u.	Electron donor	$-\Delta H$, kcal $mole^{-1}$	$-\Delta S$, e.u.
$C_2H_5NO_2$	1.5	7.1	N-Methylpyrrolidinone	4.0	10.9
$(CH_3)_2CO$	2.3	8.4	Benzene	3.2	9.0
$(C_2H_5)_5CO$	2.4	8.1	*p*-Xylene	2.5	6.7
$(C_4H_9)_2O$	2.3	5.3	Mesitylene	2.6	6.8
1,4-Dioxan	2.5	9.6	*p*-Diethylbenzene	2.7	7.8
$CH_3COOC_2H_5$	2.5	9.0	1,3,5-Triethylbenzene	2.5	7.9
$(C_2H_5O)_3PO$	3.8	9.6	*p*-Di-isopropylbenzene	3.3	10.3
$(CH_3S)_2$	0.9	6.6	1,3,5-Tri-isopropyl-benzene	2.9	9.8
$(CH_2)_4S$	2.3	10.2	18-Crown-6 ether	1.6	5.5
$(C_2H_5)_2S$	1.7	8.6	15-Crown-5 ether	4.0	7.5
$(C_2H_5)_3N$	4.1	15.2	12-Crown-4 ether	4.5	8.0

It has been established by NMR [7,8] that chloroform molecules are self-associated via C–H...Cl bonds. The self-association equilibrium constant K is low, amounting to 0.2 (mole fraction)$^{-1}$ at 25 °C, while the bond strength is $-\Delta H \cong 1$ kcal mol^{-1}. Chloroform dissolved in cyclohexane forms 1:1 complexes with the excess electron donor[7], because under these conditions the degree of its self-association is negligible. The thermodynamic characteristics of the hydrogen bonds

between chloroform and various electron donors are compared in Table 1. It is seen that the energies of the hydrogen bonds are low (2–4 kcal mol^{-1}) and that the strongest bonds are formed by amines.

The low degree of self-association of chloroform together with its tendency towards the preferential formation of 1 : 1 complexes makes it a suitable model proton donor for the study of the electron-donating properties of bases by the hydrogen bond method. The most complete data on these lines have been obtained by NMR for tertiary amines and ethers.[9] It has been shown that steric hindrance in the formation of hydrogen bonds is determined not only by the length and degree of branching of the hydrocarbon chain but also by the steric disposition of the substituents relative to the free electron pair of the heteroatom of the base. The methyl group in the β-position of the substituent hinders the approach of the proton to the electron pair. The possibility of the maximum overlap of the frontier orbitals of the proton and electron donors is then ruled out, which lengthens and weakens the hydrogen bond. For tertiary hydrogen bonds, the steric factor is most important. This is why in the series of amines there is no rigorous correlation between ΔH and Δ_C (the chemical shift due to complex formation) or $\Sigma\sigma^*$.[9]

The formation of hydrogen bonds between chloroform and phosphoryl compounds and ketones is hardly influenced by the bulk of the substituents. For this reason, a correlation is observed between ΔH and the values of $\Sigma\sigma^*$, Δ_C, or $\Delta\nu$(CH) for phosphine oxides.[10–12] Consequently the free electron pair of the donor atom, at an appreciable distance from the substituents, does not experience a steric influence by the latter.

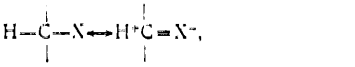
A number of studies[13–18] have been devoted to the hydrogen bonds between chloroform and π-electron donors. In the case of alkylbenzenes it was found[13] that the intermolecular interaction parameters depend in a complex manner on the electronic and steric effects of the substituents (Table 1). Contrary to expectation, the strength of the C–H...π hydrogen bonds diminishes in many instances with increase of the number of electron-donating substituents in the aromatic ring. Steric factors influence mainly the equilibrium constants. For bases whose molecules include proton-accepting centres of the π or *n* type, studies of the relative contribution of the C–H...π and C–H...*n* hydrogen bonds to the overall complex formation process are the most important.[14–18]

The proton-accepting capacity of crown-ethers has been investigated by ^{1}H NMR as a function of the number of oxygen atoms in the macroring in relation to association with chloroform.[19] The thermodynamic characteristics of the association with chloroform have been compared with data for thio- and seleno-phenols. In terms of decreasing strength of hydrogen bonds with 18-crown-6 ether, the above proton donors can be arranged in sequence Se–H ≳ S–H > C–H. An analogous sequence based on the variation of the proton-donating capacity has been observed for hydrogen bonds with electron donors of other types.[4]

For chloroform, the strength of the bond diminishes with increase of the diameter of the macroring (Table 1). In ethers with a large cavity diameter (d = 2.6 Å) the hydrogen atom involved in the bond is probably located mainly at one of the oxygen atoms. With decrease of d, the proton-accepting capacity of crown ethers increases, since the bridging hydrogen atom occupies a central or nearly central position in the cavity on formation of the complex. The possibility of an effective collective interaction of the proton charge with the dipoles of the C–O group is then ensured, which then entails the growth of the Coulombic contribution to the overall binding energy.

The proton-donating capacity of haloforms diminishes when chlorine is replaced by other halogens. The strength of the hydrogen bonds with tetrahydrofuran (THF), determined by NMR, diminishes in the sequence $Cl_3CH > Br_3CH > F_3CH > I_3CH$ ($-\Delta H$ = 3.6, 2.6, 2.4, and 1.6 kcal mol^{-1} respectively.[20] Fluoroform has a lower proton-donating capacity than chloroform and even bromoform. On the other hand, the influence of chlorine, bromine, and iodine atoms on the C–H...O hydrogen bonds corresponds to the relative electrical conductivities [sic]. The above data agree with the results of calculations by the CNDO/2 method.[21] We may recall that the strength of the hydrogen bonds between hydrogen halides and various electron donors diminishes in conformity with the variation of electronegativity on passing from F to I.[22]

There is no unaminous view in the literature about the causes of the "anomalous" influence of fluorine atoms on the proton-donating capacity of substituted methanes. It has been suggested that the deviations are caused by the greater polarisability of C–Cl bonds compared with C–F.[23] However, the main contribution to the energy of weak hydrogen bonds comes from the polarisation component and not from the Coulombic component.[24] Furthermore, the polarisability of the H–F bond is also lower than that of the H–Cl bond but hydrogen fluoride is a stronger proton donor. We believe that the explanation put forward by Creswell and Allred[20] is acceptable. According to these workers, the decrease of ΔH on passing from chloroform to fluoroform is due to the fact that, owing to the absence of *d* orbitals in fluorine atoms, resonance of the type



as a result of which the positive charge on the hydrogen atom and the polarity of the C–H bond increase, is impossible. Furthermore, the decrease of the positive charge on the hydrogen atom in fluoroform and of the proton-donating capacity of the latter, can be induced by the +*M* effect of the free electron pairs of the halogen, which is a maximum in the case of fluorine.[25] The last two factors should play a decisive role in the variation of the strength of the C–H...B bonds whose energy is determined mainly by the electrostatic interaction. The above treatment is consistent with the results of calculations by the CNDO/2 method, according to which the charge on the hydrogen atom in the chloroform molecule is much greater than in the fluoroform molecule.[25,26]

Compared with the chlorine atom, the CF_3 substituent generates a much greater positive charge on the hydrogen atom of the C–H group.[27,28] CH acids with the trifluoromethyl substituent therefore exhibit a greater proton-donating capacity. For example, the enthalpy of formation of the hydrogen bond with methylpyrrolidinone (in kcal mol^{-1}) is 4.0 for chloroform[7] and 4.7 for $CF_3CHClBr$;[30] in the case of dimethyl sulphoxide (DMSO) the corresponding values are 1.6 for chloroform[31] and 5.6 for $(CF_3)_3CH$.[29]

III. HYDROGEN BONDS INVOLVING CH GROUPS POLARISED BY ELECTRON-ACCEPTING SUBSTITUENTS

Hydrogen bonds involving CH groups polarised by powerful electron-accepting substituents such as CN, NO_2, CO_2R, SO_2R, etc. are very common. In the first place we may note that the above substituents include atoms with proton-accepting capacity. The corresponding CH acids can therefore be self-associated. However, according to NMR data the stability of the self-associated species of monosubstituted methanes is low and amounts to 0.6–1.8 kcal mol^{-1}.[30,31]

Judging from the inductive σ constants, substituents such as the cyano-, nitro-, and sulpho-groups should increase the proton-donating capacity to a greater extent than the halogens. Indeed, the introduction of the CN group into mono- and dihalogenomethanes leads to a greater shift of the stretching vibration frequency of the C–H bond than the introduction of a second or third halogen atom.[3] The enthalpies of formation of the hydrogen bonds of CH_2Cl_2, $CHCl_3$, and $CHCl_2CN$ with dioxan are 1.3, 2.4, and 3.5 kcal mol^{-1} respectively.[3] Nitromethane and chloroform form with acetone hydrogen bonds of similar strength (2.1 and 2.3 kcal mol^{-1}),[7,32] while the strength of the hydrogen bond involving 1,1-dinitroethane varies in the range 3–7 kcal mol^{-1} depending on the strength of the electron donor.[33]

However, the available data make it possible to follow only the qualitative aspect of the influence of the nature of substituents on the properties of the C–H...B hydrogen bonds. Rigorous quantitative correlation between the association parameters and the electron-accepting properties of substituents are as a rule absent. For example, according to Slasinski et al.,[34] it is possible to set up the following series based on the influence of the substituents on the association constant of methane derivatives with hexamethyl phosphoramide (HMPA): $CN \approx NO_2 > SCN > O_2NC_6H_4 > F$, Cl, Br $> CON(CH_3)_2 > CO_2R > C_6H_5$. Overall, it resembles the sequence in the variation of the σ_I, but the correlation between $\lg K$ and σ_I is very rough. There exist several possible causes of its breakdown. The proton-donating capacity of CH groups depends significantly on steric conditions, since the electron-accepting groups are in the immediate vicinity of the reaction centre. The negative charge concentrated on them hinders the approach of the base molecule to the proton of the CH group. Furthermore, with increase of the number of substituents, there is a possibility that the saturation effect, which is a progressive decrease of the substituent influence on the polarity of the C–H bond, may be manifested.[35]

quantum-chemical calculations,[25] the CF_3 substituent increases the charge on the hydrogen atom of the CH group to a greater extent than the NO_2 substituent.

Thus it is fairly difficult to predict the proton-donating capacity of the CH group polarised by electron-accepting substituents. The use of inductive constants does not yield the desired result. In individual systems it is possible to explain reasonably the experimental behaviour by resorting to data for the charges on the reaction centre.

The dependence of the characteristics of the hydrogen bonds of di- and tri-substituted methanes with electron donors of different nature on the CH acidity has been analysed.[36,37] For the hydrogen bonds of R_2CH_2 with pyridine, a parallel variation with the proton-donating capacity and acidity is observed in the main; however, in the case of DMSO the values of ΔH are almost independent of the pK_a. Malononitrile forms the weakest bond with DMSO, while in relation to pyridine its proton-donating capacity is consistent with the acidity. The reason for the above anomaly is that, apart from the hydrogen bonds, $(NC)_2CH_2$ forms dipole–dipole associated species with DMSO (according to infrared spectroscopic data[37]) by interaction between the localised dipoles of the CN and SO groups. According to the results of calculations in terms of the CNDO/2 approximation, the electron-accepting properties of the CN substituent and the proton-donating capacity of the CH group are sharply diminished in associated species of the dipole–dipole type.[38]

On passing to trisubstituted methanes (Table 3), the increase of acidity is accompanied by the enhancement of the proton-donating capacity. However, in the series of acids $HC(Y)(SO_2CH_3)SO_2C_6H_4X$ there is no single dependence of ΔH on pK_a.

Table 2. Thermodynamic characteristics of the hydrogen bonds between trisubstituted methanes and DMSO in carbon tetrachloride.[29]

R_3CH	σ_I^*	$-\Delta H$, kcal $mole^{-1}$	Δ_C, p.p.m.
{$(CF_3)_3$}CH	0.42	5.6	2.60
$(CF_3)_2$CH{NO_2}	0.63	4.8	2.34
$(CF_3)_2$CH{CN_2}	0.58	4.7	2.23
$(CF_3)_2$CH{$COOCH_3$}	0.32	3.3	1.47
{CH_3}{$CH(NO_2)_2$}	0	2.2	0.72

*The values of σ_I are quoted for the groups shown in braces.

Table 3. Thermodynamic characteristics of the hydrogen bonds between trisubstituted methanes $HC(COY)(SO_2CH_3)$. $(SO_2C_6H_4X)$ and DMSO and acetone (at 40 °C).[37]

X	Y	pK_a (CH_3OH)	Acetone			DMSO		
			$-\Delta H$, kcal $mole^{-1}$	$-\Delta S$, e.u.	K, (mole fraction)$^{-1}$	$-\Delta H$, kcal $mole^{-1}$	$-\Delta S$, e.u.	K, (mole fraction)$^{-1}$
Cl	C_6H_5	4.77	2.5	5.0	4.6	3.3	5.5	13.6
H	C_6H_5	5.32	2.3	4.3	4.2	3.4	6.1	12.0
CH_3	C_6H_5	5.81	2.4	5.1	4.0	3.0	5.1	10.5
Cl	OC_2H_5	5.24	2.7	5.1	6.2	2.6	4.1	8.0
H	OC_2H_5	6.06	2.3	5.6	4.5	2.6	4.5	7.0
CH_3	OC_2H_5	6.36	2.5	5.3	4.7	2.6	4.6	7.0

In our view, the magnitude of the charge on the hydrogen atom of the CH group, determined by quantum-chemical calculations, should characterise the proton-donating capacity of CH acids more fully than the inductive constants of the substituents. Analysis of the results presented in Table 2 provides a definite confirmation of the above hypothesis. Evidently, the replacement of CF_3 by NO_2 weakens the hydrogen bond despite the fact that the nitro-group has a greater electron-accepting inductive effect than the trifluoromethyl group. The reason for this is that, in conformity with

The change in the nature of the substituent Y adjoining the reaction centre alters the proton-donating capacity in parallel with the equilibrium acidity. On the other hand, the effects of the substituent X remote from the reaction centre on the proton-donating capacity and on thermodynamic acidity are not correlated. The absence of a general correlation between the proton-donating capacity of R_3CH in hydrogen bonds and acidity reflects the fact that the effects of the substituents in the molecule and in the carbanion are transmitted to the reaction centre via mechanisms of different types. In the

acid, the properties of the C–H bond are mainly determined by inductive effects, while in the carbanion there is a possibility of a mesomeric interaction.

IV. THE PROTON-DONATING CAPACITY OF UNSATURATED HYDROCARBONS

The proton-donating capacity of CH groups depends not only on the number and properties of electron-accepting substituents but also on the character of the hybridisation of the valence orbitals of the carbon atom.[3] With increase of the amount of *s* character, the proton-donating capacity also increases in view of the increase of the electronegativity of carbon and the polarity of the C–H bond. An increase of the positive charge on the hydrogen atom is observed in the series of groups

$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}} < \mathrm{H{-}\overset{|}{\underset{|}{C}}{=}} < \mathrm{H{-}C{\equiv}}$$ (Ref.26).

The introduction of electron-accepting substituents naturally increases the proton-donating capacity of unsaturated compounds. Thus the substituents R can be arranged in the following sequence in terms of their influence on the constant for the association of $R_2C{=}CHR$ with HMPA:[34] CN ≈ NO_2 > Cl > Br > C_6H_5. An analogous sequence of substituent effects was presented above for methane derivatives.

It has been shown by NMR [30] that trichloroethylene is self-associated via hydrogen bonds of the type C–H...Cl. The stability of the species produced by its association with various electron donors varies from 1.4 kcal mol^{-1} for acetone to 4.5 kcal mol^{-1} for triethylamine (TEA).[32] The CH groups of substituted benzenes with electron-accepting substituents also exhibit proton-donating properties.[34,39,40] In the aldehydes the capacity of the hydrogen atom of the CHO group to form hydrogen bonds with DMSO, phosphine oxides, and pyridine has been observed for trichloroacetaldehyde ($-\Delta H$ = 2.4–5.2 kcal mol^{-1}).[41,42]

Acetylenic compounds form hydrogen bonds involving the π electrons of the triple bond. The enthalpy of self-association is 1.5–2.0 kcal mol^{-1}. The hydrogen bonds of monoalkylacetylenes with various electron donors are characterised by the enthalpies $-\Delta H$ = 1–3 kcal mol^{-1}.[43,44] The influence of electron-accepting substituents on the proton-donating capacity of $RC{\equiv}CH$, estimated from the increase of the chemical shift on association with acetone, increases in the following sequence of substituents R: COOH < CHO < $COCH_3$ < $COOC_2H_5$ < CN,[45] while the corresponding sequence for association with pyridine is $HO(CH_2)_2$ < $CH_3OC(CH_3)_2$ < $HOC(CH_3)_2$ < C_6H_5 < $C_6H_5OCH_2$;[46] estimation of this influence from the variation of the *K* in mixtures with HMPA led to the sequence C_6H_5 (0.15) < $BrCH_2$ (0.53) < $COOC_2H_5$ (1.66) < CN (12.1).[34] The association of phenylacetylene with ethers and thioethers has been investigated by NMR and infrared spectroscopy.[47] The values of *K* obtained by different methods agree satisfactorily. A correlation is observed between lg*K* and the Δν(CH).

In concluding the discussion of the properties of the C–H...B hydrogen bonds, we may note studies[23,48–49] in which the nature of the hydrogen bonds involving CH acids was investigated by quantum-chemical methods. Analysis of the redistribution of electron density (charge shift and transfer) on formation of the C–H...B hydrogen bonds showed that the bonds do not differ from O–H...B or N–H...B. The maximum contribution to the energy of the C–H...B bonds comes, as for O–H...B bonds, from the electrostatic interaction, while the polarisation contribution and the contribution due to charge transfer play a secondary role.

V. CH ACIDITY (GENERAL POSTULATES)

The reactivity of CH acids is characterised by the kinetic (*k*) and equilibrium or thermodynamic (pK_a) acidities. These parameters are linked by the Brønsted relation:

$$\lg k_{+(-)} = \alpha(\beta)\Delta pK_a + \mathrm{const}, \qquad (1)$$

where

$$\Delta pK_a = pK_a(BH^+) - pK_a(CH)$$

and α and β are the reaction constants for the forward and reverse proton transfer reactions:

$$C{-}H + B \underset{k_-}{\overset{k_+}{\rightleftarrows}} C^- + HB^+. \qquad (2)$$

According to Eqn.(1), the rate of elimination of the proton should increase with increasing strength of the acid or base. The values of α and β are usually constant for a series of compounds of similar structure and α + β = 1.

The Brønsted correlation is a consequence of the fundamental principle of the linear relation between the free energies of activation and of the equilibrium reaction: $\Delta\Delta G^{\neq} = \alpha\Delta\Delta G$. If it is assumed that the entropy change in the reaction series can be neglected, the above expression assumes the form

$$\Delta E = \alpha\Delta Q, \qquad (3)$$

where *E* and *Q* are the activation energy for the proton transfer reaction and the heat of the latter. It is noteworthy that the constancy of α is maintained within a relatively narrow range of values of ΔQ or ΔpK_a. For highly exothermic reactions ($\Delta pK_a \gg 0$), the activation energy for the forward process is low and α → 0 and β → 1. On the other hand, for highly endothermic reactions ($\Delta pK_a \ll 0$) we have α → 1 and β → 0. In the range of intermediate values of ΔpK_a the values of α and β are between 0 and 1 and α + β = 1. The extent of the transitional region can be estimated with the aid of the Marcus semiquantitative theory,[50] according to which the relation between the free energies of activation and of the equilibrium reaction includes the so-called internal barrier to reaction, i.e. the value of $\Delta G^{\neq}$ corresponding to $\Delta G = 0$:

$$\Delta G^{\neq} = (1 + \Delta G/4\Delta G_0^{\neq})^2 \cdot \Delta G_0^{\neq} \qquad (4)$$

It follows from Eqn.(4) that

$$\alpha = d\Delta G^{\neq}/d\Delta G = \frac{1}{2}(1 + \Delta G/4\Delta G_0^{\neq}), \qquad (5)$$

$$d\alpha/d\Delta G = (8\Delta G_0^{\neq})^{-1}. \qquad (6)$$

Consequently, for symmetrical proton-exchange reactions ($\Delta G = 0$), we have α = 0.5. With increase of the internal activation barrier, the curvature of the function $\alpha = f(\Delta G)$ or $\alpha = f(\Delta pK_a)$ diminishes and the range of values of ΔG and ΔpK_a in which α varies from 0 to 1 should broaden.[51]

The Hammond–Leffler postulate,[52,53] according to which α reflects the energy symmetry of the transition state, imparts a physical significance to the reaction constant α(β). For exothermic reactions (α < 0.5), the structure of the transition state resembles that of the initial reactant, while for endothermic reactions (α > 0.5) it resembles that of the product, i.e. α reflects the degree of proton transfer in the transition state of reaction (2). However, it is not yet clear whether there is a quantitative relation between α and the length or order of the bond in the C...H...B transition state.

Definite ideas concerning the structure of the transition state have arisen from the study of the kinetic isotope effect in proton transfer reactions.[1,2] It has been established experimentally that the dependence of k_H/k_D on ΔpK_a is

represented by a bell-shaped curve and reaches a maximum in the region of $\Delta pK_a = 0$, i.e. for systems to which a symmetrical transition state corresponds according to the Hammond–Leffler postulate.

On the basis of the theoretical postulate examined above, Eigen, who carried out extensive studies on protolytic reactions, proposed a classification of acids,[53] within the framework of which the large group of OH acids is regarded as "normal". The following are the features believed to be characteristic of the normal behaviour of acids:

(1) the rate of proton transfer in the thermodynamically favourable direction is limited by diffusion and is independent of ΔpK_a, i.e. $\alpha = 0$;

(2) in the reverse, slow direction, the reaction is characterised by the maximum sensitivity of the rate to ΔpK_a, i.e. $\alpha = 1$;

(3) the values of α and β differ from 0 to 1 respectively over a narrow range of values of ΔpK_a close to zero;

(4) in the transition state the proton has been almost fully transferred to the acid or base and the observed kinetic isotope effects are therefore insignificant.

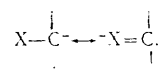
Deviations from the "normal" behaviour are characteristic of many CH acids. For example, the proton transfer even in the thermodynamically favourable direction is much slower than in the diffusion limit. Such results led to the description of CH acids as "pseudoacids". However, as will be seen below, many CH acids behave "normally", i.e. similarly to OH acids.

VI. THE ACIDITY OF HALOGEN-SUBSTITUTED HYDROCARBONS

Saturated hydrocarbons exhibit an extremely low acidity ($pK_a = 40$ for methane). In conformity with the Brønsted relation, proton transfer only to strong bases is observed and the reaction is slow.[1] The introduction of halogens sharply increases and acidity of hydrocarbons. Isotope exchange proceeds at measurable rates; alkaline but not acid catalysis is effective. The kinetics and equilibria of reactions involving proton transfer from halogen-substituted CH acids have been studied in relatively fair detail.[55–58] A general conclusion reached in the studies quoted is that a "normal" behaviour is characteristic of CH acids of this type. Thus the rate of isotope exchange involving fluoroform and chloroform in H_2O–DMSO mixtures increases, while the activation energy diminishes with increasing basicity of the medium. The kinetic results are described by the Brønsted relation ($\alpha = 0.98$). The rates of proton transfer to the carbanion are virtually the same and approach the diffusion limit. The transition state in the acid ionisation reaction probably resembles the product. The low kinetic isotope effects $k_H/k_D \leqslant 2.5$ are consistent with this hypothesis.[55]

Analogous results have been obtained for the deuterium–hydrogen exchange reactions of polyfluoro-substituted CH acids.[56] In these systems too the kinetic isotope effect was small (2.1–2.5). The transfer of the proton of the C–H bond to the methoxide ion in alcoholic solution has a high activation barrier (20–28 kcal mol^{-1}). These data indicate the antisymmetric structure of the transition state. The effect of the substituents on the equilibrium and kinetic acidities of the compounds discussed is the same, since we have $K_a \cong k_+$ when $k_- = \text{const}$.

It is noteworthy that the effect of the halogens on the equilibrium and kinetic acidities of the C–H bonds is not correlated with their electronic acitivity (Table 4) [57,58] and is probably not determined solely by the inductive effects of the substituents. According to Hine et al.,[57] the increase of acidity in the series of haloforms is due to the stabilisation of the carbanion as a consequence of the involvement of the *d* orbitals of the substituent in the delocalisation of the free electron pair:



Such resonance is impossible for fluorine owing to the absence of *d* orbitals and fluoroform is therefore least acidic. On the other hand, the increase of acidity on passing from chlorine to iodine is attributed to the greater polarisability of the orbitals of the latter.

Table 4. The rates and activation parameters of deuterium exchange involving halogenomethanes under the conditions of alkaline catalysis in aqueous solutions.[57,58]

Hal_3CD	10^4k, litre mol^{-1} s^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	pK_a
F_3CD	$1.8\cdot10^{-5}$	32.0	18.0	27
Cl_2FCD	0.89	25.9	17.7	18
$BrClFCD$	21	24.3	18.3	15
Cl_3CD	47	23.5	17.0	15
Br_2FCD	180	—	—	13
Cl_2ICD	275	22.1	15.3	13
Cl_2BrCD	290	—	—	13
$ClBr_2CD$	1435	21.3	15.6	12
Br_3CD	5790	20.3	15.0	11
I_3CD	6010	20.2	14.5	11

According to ideas developed in a number of studies,[24,59,60] the destabilising +*M* effect, induced by the repulsion between the *n* electrons of the halogens and the free electron pairs of the carbanion and, evidently, to a much lesser extent also the binding electrons of the CH group in the acid, exerts the main influence on the acidity of haloforms. This effect increases on passing from iodine to fluorine, since the amount of *p* character of the *n* electrons increases in the same sequence and their energy diminishes with decrease of the atomic radius. The changes enumerated above promote the growth of the capacity of halogens for conjugation. The observed acidity series for haloforms is fully consistent with the hypothesis of the destabilising +*M* effect of the substituents.

However, the mechanism of the influence of fluorine atoms on the properties of CH acids may vary with the position of the substituent relative to the reaction centre.[56,60] For example, on passing from fluoroform to $(CF_3)_3CH$, an increase of the kinetic acidity almost by nine orders of magnitude is observed, although the inductive constants for CF_3 and F are virtually identical. Evidently, the fluorine atoms in the β-position interact with the reaction centre only via the inductive mechanism and increase the CH acidity in conformity with their high electronegativity. On the other hand, the destabilising +*M* effect remains dominant for the fluorine atoms in the α-position (see above).

Table 5 presents data[60] which make it possible to follow the dependence of the type of influence of the fluorine atoms on the acidity as a function of their position relative to the reaction centre. It is clearly seen that only F atoms remote from the CH group increase the acidity (compounds 2, 4, and 5), while the F atoms in the α-position reduce the acidity even relative to the phenyl substituent.

Thus halogen-substituted hydrocarbons belong to "normal" acids in terms of Eigen's classification. The variation of their properties as a function of the nature or position of the halogen can be accounted for satisfactorily by the competing inductive and destabilising +*M* effects.

Table 5. The relative rates of deuterium exchange involving the compounds $(CF_3)_2CHX$ in the DMSO–MeOH system catalysed by TEA (at 37 °C).[60]

No.	X	k_{rel}	pK_a
1	C_6H_5	1	17.9
2	CF_3	4300	7
3	F	0.86	18
4	*m*-FC_6H_4	18.4	—
5	*p*-FC_6H_4	1.54	—
6	Cl	651	12.6
7	Br	2227	11.5
8	I	154	13.7

VII. THE INFLUENCE OF ELECTRON-ACCEPTING GROUPS ON THE PROPERTIES OF CH ACIDS

Electron-accepting substituents can be divided into two types. The first includes the CN, SO_2R, etc. substituents, interacting with the reaction centre of the carbanion mainly via the inductive mechanism. The second includes the COOR, COR, C_6H_5, etc. substituents, stabilising the carbanion via the conjugation mechanism. As will be seen below, the difference between the mechanisms of the influence of substituents is an important cause of the "anomalies" characteristic of many CH acids.

The CN and SO_2R ($\sigma_I = 0.58$) groups are some of the most powerful electron-accepting substituents. The acidity of the corresponding disubstituted methanes varies in the range $pK_a = 11-15$. The acid strength of the corresponding trisubstituted methanes is comparable to that of inorganic acids; for example, $pK_a = 0$ for cyanoform. Table 6 presents the results of kinetic studies of trisubstituted methanes of the type $HC(X)(SO_2R)_2$ and $HC(X)(CN)_2$.[61-63] Their analysis together with the results obtained in other studies[64,65] showed that Brønsted correlations are observed for sulpho- and cyano-methanes with X = H or alkyl and α close to unity on varying both the CH acid and the base. The rates of protonation of the carbanion are close to the rate limited by diffusion. The deprotonation of these acids is accompanied by small isotope effects: $k_H/k_D = 1.5$.[61,64,66]

Thus disulphones and dinitriles with alkyl substituents behave in deprotonation reactions as "normal" acids. Compounds with phenyl or aryl substituents are exceptions in both systems. Thus, for similar pK_a values, the kinetic acidity of the compounds with the C_6H_5 group is significantly lower (Table 6). It is noteworthy that the introduction of the phenyl group diminishes both k_+ and k_-. The above "anomalies" are not exceptional. They are characteristic also of other sulphones or nitriles containing a substituent capable of conjugation.

A significant difference between sulphones and nitriles, on the one hand, and compounds with the NO_2, COOR, COR, etc. groups, on the other, is that, while the equilibrium acidities are comparable, the latter compounds exhibit an appreciably lower kinetic acidity (Table 7) and also relatively low rates of protonation of the carbanion. Furthermore, in contrast to acids with substituents of the type Hal, CN, SO_2R, etc., the nature of the substituents in these compounds influences the rates of both the foward and reverse reactions. The coefficients α and β differ from 0 to 1 over a wide range of values of ΔpK_a. For example, the relation between $\lg k_+$ and ΔpK_a, which is common to a large number of ketones, ethers, ketoethers, and various bases, is represented by a smooth curve whose slope varies almost by a factor of 2 when pK_a changes by 25 units.[2] The kinetic isotope effect reaches a maximum in the region of $\Delta pK_a = 0$ ($k_H/k_D = 10$) and then gradually diminishes to 2 both in the region where $\Delta pK_a \cdot 0$ and the region where $\Delta pK_a \cdot 0$.

Table 6. Kinetic characteristics of the reactions involving proton transfer from disulphones and dinitriles of the type $XCH(Y)_2$ to water.[61-63]

X	Y	$10^5 k_+$, litre mol^{-1} s^{-1}	$10^{-10} k_-$, litre mol^{-1} s^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	pK_a
H	$C_6H_5SO_2$	408	2.1	—	—	11.21
C_6H_5	$C_6H_5SO_2$	1.06	0.045	—	—	12.20
H	$C_2H_5SO_2$	30.7	1.6	—	—	12.20
H	CH_3SO_2	20.6	2.3	—	—	12.55
CH_3	$C_6H_5SO_2$	1.15	2.1	—	—	13.76
CH_3	$C_2H_5SO_2$	0.063	0.73	—	—	14.56
H	CN	51.6	0.26	15.6	−20.4	11.1
t-C_4H_9	CN	0.07	0.4	18.5	−20.7	13.1
p-$NO_2C_6H_4$	CN	$0.9 \cdot 10^{-4}$	—	21.0	−30.0	13.1

Table 7. The rate and equilibrium constants for the dissociation of CH acids in water (25 °C).[67]

CH Acid	K_a	k_+, s^{-1}	k_-, litre mol^{-1} s^{-1}
CH_3NO_2	$6.1 \cdot 10^{-11}$	$4.3 \cdot 10^{-8}$	$6.8 \cdot 10^{3}$
$CH_3COCH_2CO_2CH_3$	$2.1 \cdot 10^{-11}$	$1.2 \cdot 10^{-3}$	$5.8 \cdot 10^{7}$
$CH_3CH(COCH_3)_2$	$1.0 \cdot 10^{-11}$	$8.3 \cdot 10^{-5}$	$8.3 \cdot 10^{6}$
$CH_2(CN)_2$	$6.5 \cdot 10^{-12}$	$1.5 \cdot 10^{-4}$	$2.3 \cdot 10^{7}$

It has been shown[68,69] that, in the proton exchange reactions of toluene, diphenylmethane, and their derivatives catalysed by bases of different strengths, the coefficient α varies in the range 0.31–0.75 and increases with decrease of the strength of the base. It is believed[68,69] that this is associated with the fact that the ionisation of CH acids of the above type entails a change in the hybridisation of the atomic orbitals of the carbon atom. On passing to the anion, the amount of *p* character of the orbital of the free electron pair increases, which stabilises the anion as a result of p–π conjugation with the electrons of the benzene rings.

Since the maximum overlap of the orbitals of the free electron pair and the substituent is possible for a planar configuration of the anion, the dissociation of CH acids of the type considered involve significant structural rearrangements promoting the delocalisation of the charge in the carbanion. Structural reorganisations require an energy expenditure and lead primarily to an increase of the internal activation barrier [see (Eqn.(4)]. This is why k_+ and k_- decrease and the range of ΔpK_a values in which α and β vary from 0 to 1 expands [see Eqn.(5)].

The conjugation effect, which increases the stability of the cation, does not influence to an equal extent the thermodynamic and kinetic acidities. The stabilisation of the carbanion leads to an increase of the strength of the acid and of the rate of its ionisation. However, the k_+ are then smaller than the expected value corresponding to an increase of the equilibrium acidity without taking into account the rehybridisation of the bonds and the delocalisation of the charge.[1]

One may expect that $\Delta G_0^{\neq}$ will increase and α will diminish in the region of positive ΔG with increase of the capacity of the substituents for delocalising the charge of the carbanion in the sequence $SO_2R < CN < COOR < COR < NO_2$ [70,71] [see Eqn.(5)]. The experimental results[72] presented in Table 8 are consistent with this hypothesis.

Table 8. The Brønsted coefficients for the ionisation of certain CH acids when the substituents X in the acid and in the base are varied.[72]

CH acid	Base	α
$C_6H_5CH_2CHCOCH_3CO_2C_2H_5$	XCO_2^-	0.44
$XC_6H_4CH_2CHCOCH_3CO_2C_2H_5$	$CH_3CO_2^-$	0.77
$C_6H_5CH_2CH(COCH_3)_2$	XCO_2^-	0.44
$XC_6H_4CH_2CH(COCH_3)_2$	$CH_3CO_2^-$	0.58
$C_6H_5CH_2CH(CN)_2$	XCO_2^-	1.00
$XC_6H_4CH_2CH(CN)_2$	$ClCH_2CO_2^-$	0.98

Thus the deviations of acids with substituents of the type C_6H_5, COOR, etc. from the "normal" behaviour are associated primarily with the fact that the conjugation effect makes a significant but not decisive contribution to the stabilisation of the carbanion.

The "normal" behaviour is characteristic of acids with substituents of the type CN, SO_2R, alkyl, and Hal, since their ionisation is not accompanied by a significant delocalisation of the charge and the carbanion is stabilised mainly via the inductive mechanism. Naturally, one cannot rule out the involvement of interactions of another type in stabilisation but for the CN and SO_2R substituents the contribution of resonance effects is small.[73]

VIII. THE "NITROALKANE ANOMALY"

Those CH acids whose behaviour can be regarded as "normal" or "anomalous" within the framework of Eigen's classification were examined above: the properties of both types of such acids are described by the Brønsted relation. Typical examples of systems whose behaviour does not obey the Brønsted equation are discussed below and the possible causes leading to the breakdown of the Brønsted relation are analysed.

Table 9 compares the acid properties of various diketones.[67,74] The fact that the replacement of the CH_3 group by CF_3 leads to an increase of the equilibrium acidity in conformity with the high electronegativity of the fluorine atom but the kinetic acidity diminishes at the same time is noteworthy. The coefficient $\alpha < 0$ for this system, i.e. has an "anomalous" value.

Anomalous values of the Brønsted coefficient ($\alpha < 0$ and $\alpha > 1$) are most characteristic of CH acids containing the nitro-group. Thus the equilibrium acidity of nitroalkanes increases in the sequence

$$CH_3NO_2\ (10.2) < C_2H_5NO_2\ (8.5) < (CH_3)_2CHNO_2\ (7.7)$$

(the pK_a are given in brackets), but the relative rates of abstraction of protons by hydroxide ions diminish (111 : 18 : 1) in the same sequence. The coefficients $\alpha = -0.7$ and $\beta = 1.7$ are anomalous.[75] The ionisation of alkyl-substituted nitromethanes of the type R_2CHNO_2 (where R = H, CH_3, C_3H_7, iso-C_3H_7, or t-C_4H_9) is also characterised by negative values of α.[71]

Table 9. The equilibrium and kinetic acidities of various diketones in aqueous solutions.[14,67]

CH Acid	pK_a	$10^5 k_+^T$, s^{-1}	$10^2 k_+^H$, s^{-1}	k_-^H, litre mol^{-1} s^{-1}
$(CH_3CO)_2CH_2$	8.99	66.5	1.6	$1.7 \cdot 10^7$
$CF_3COCH_2COCH_3$	6.78	33.3	1.5	$7.5 \cdot 10^2$
$(CF_3CO)_2CH_2$	5.3	15.1	—	—
$CH_3COCH_2COC_6H_5$	9.4	—	1.1	$2.7 \cdot 10^7$
$CF_3COCH_2COC_6H_5$	6.8	—	0.8	$5.5 \cdot 10^4$

Anomalies of another kind are also characteristic of nitrocompounds: the sensitivity of the kinetic acidity to the influence of substituents is greater than that of the equilibrium acidity, i.e. $\alpha > 1$. For example, $\alpha = 1.67$, 1.61, 1.42, and 1.56 have been found for nitroalkanes having the formulae

$R(CH_2)_3NO_2$, $ArCH_2CH(CH_3)NO_2$, $ArCH(CH_3)NO_2$ and $ArCH_2NO_2$

respectively.[71,76] The reaction constant diminishes somewhat after the introduction of the chlorine atom ($\alpha = 1.23$ for $RCHClNO_2$), but the anomaly persists.[77,78] The above systems have been investigated in water and aqueous alcoholic solution. It must also be emphasised that all systems with $\alpha > 1$ included a fixed base. If the base is varied for the same nitroalkane, then the Brønsted coefficient returns to the range within the "normal" limits, i.e. $0 < \alpha < 1$.[79,80]

The hypothesis of a relation between α and the degree of proton transfer in the transition state was discussed above. The relation implies that the influence of the substituents on the transition state is intermediate between their influence on the CH acid and the carbanion. It is quite evident that in the case of nitroalkanes and similar systems, for which $\alpha < 0$ or $\alpha > 1$, such a hypothesis lacks significance.

We shall consider the general characteristics of systems for which the Brønsted coefficient has an anomalous value. In the first place we shall note that in both cases ($\alpha < 0$ and $\alpha > 1$) the effect of the substituents on k_+ and k_- is qualitatively the same. The difference is that, when $\alpha > 1$, the substituent decreases the energy of the transition state to a greater extent than that of the anion (Fig.1, curve *b*), i.e. k_+ increases faster than k_-. When $\alpha < 0$, the substituent increases the energy of the transition state but decreases that of the anion (Fig.1, curve *c*), i.e. k_- decreases to a greater extent than k_+.

The question of the causes of the anomalies described above is controversial. The influence of substituents is manifested via various effects, which in their turn make non-equivalent contributions to the energies of the transition state and the

carbanion. Thus the conjugation effect should be fully manifested only for the carbanion and can be virtually absent in the transition state. On the basis of this hypothesis, it is possible to account for the inverse relation between the kinetic and thermodynamic acidities in the series of methylnitroalkanes. The decrease of the kinetic acidity after the introduction of the CH_3 group is induced by the electron-donating inductive effect of this group, while the increase of the equilibrium acidity is caused by the stabilisation of the anion by the hyperconjugation effect.[81]

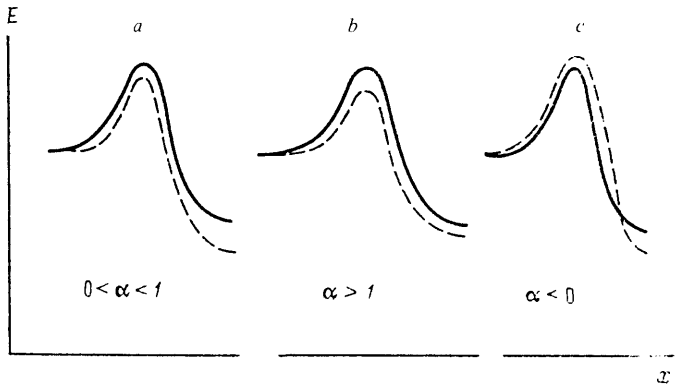
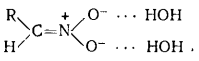


Figure 1. The effect of the introduction of a substituent on the variation of the potential energy E along the proton transfer reaction coordinate x characterised by the normal (a) and "anomalous" (b and c) values of α (continuous line—without a substituent; dashed line—with a substituent).

In aqueous alcoholic solutions specific intermolecular interactions are important apart from the intramolecular electronic effects. Solvation can stabilise the transition state and the carbanion to different extents. For example, the nitroalkane anions are stable in the ground state by virtue of solvation with which the formation of relatively stable hydrogen bonds is associated:



In this case electron-accepting substituents increase the electronic stability of the carbanion but diminish its capacity for the formation of hydrogen bonds with the solvent. Thus the influence of substituents on the anion is smoothed out. The electron-donating methyl groups promote the solvation of the anion and also increase its stability as a result of intramolecular hyperconjugation effects (see above).

In the transition state the partial negative charge is localised on the carbon atom and the solvation effects are insignificant.[79,82] The electronic effects of the substituents in the acid and in the transition state should therefore play the major role in determining the activation energy for the abstraction of a proton.[82]

The important role of solvation effects in the manifestation of "anomalies" is indicated by the following results. On passing from $ArCH_2NO_2$ to $ArCHClNO_2$, the quantity α diminishes from 1.56 to 1.23,[77,78] while for compounds of the type $ArCH(NO_2)_2$ the normal value is attained ($\alpha = 0.75$), because polynitroalkane anions hardly form hydrogen bonds with this solvent.[83]

On passing from aqueous solutions to the aprotic solvent DMSO and in the gas phase a decrease of the "anomalous" influence of the methyl groups on the equilibrium acidity of nitro-compounds is observed (Table 10).[83,84] However, the sequence of the changes in acidity with substitution remains common to all three cases. Consequently the anomaly in the constants K_a for the acids considered is caused not only by solvation but also by hyperconjugation effects.

Table 10. The change in the thermodynamic acidity $\Delta pK_a = pK_a^H - pK_a^{CH_3}$ in water, DMSO, and the gas phase on substitution of the hydrogen in nitromethane by the methyl group.[84]

CH Acid	H_2O	DMSO	Gas phase
CH_3NO_2	0.00	0.00	0.00
$CH_3CH_2NO_2$	1.80	0.68	0.5
$(CH_3)_2CHNO_2$	2.96	0.79	1.2

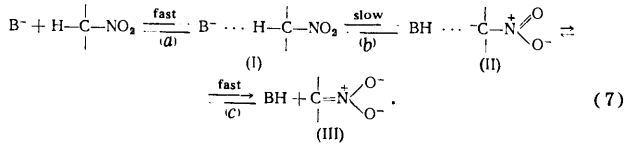
For compounds having the formula $ArCH_2NO_2$, the transition from H_2O to DMSO leads to a decrease of α from 1.56 to 0.92.[82] In DMSO the rate of dissociation decreases sharply and the heat of activation falls, which is believed[24] to be associated with the fact that the basicity of the medium increases with increasing DMSO concentration. For the given fixed acid $C_7H_5CH_2NO_2$, the change in base strength in the H_2O–DMSO mixture leads to $\alpha = 0.58$. Consequently even in the aprotic solvent the values of α determined for a fixed acid (0.58) or base (0.92) are not the same. On passing from H_2O to DMSO, the anomaly does not disappear in this system, although the extent to which it is manifested diminishes.

A formal explanation of the "nitroalkane anomaly" has been proposed by Marcus.[50,85] We may recall that, when the internal activation barrier is constant within the limits of the reaction series, α is specified by Eqn.(5) and is within the normal limits ($0 < \alpha < 1$) subject to the condition that $|\Delta G| \leq |4\Delta G_0^{\neq}|$. A change in the nature of the base should not influence $\Delta G_0^{\neq}$, so that for a fixed nitroalkane the Brønsted relation holds when the base is varied. On the other hand, when the introduction of a substituent into the acid alters the internal activation barrier, then α is specified by the expression

$$\alpha = \frac{1}{2}\left(1 + \frac{\Delta G}{4\Delta G_0^{\neq}}\right) + \left[1 - \left(\frac{\Delta G}{4\Delta G_0^{\neq}}\right)^2\right]\frac{d\Delta G_0^{\neq}}{d\Delta G},$$

whose second term can influence α significantly. The change in $\Delta G_0^{\neq}$ within the limits of the reaction series is possible either as a result of a structural reorganisation of the transition state or as a consequence of solvation effects.

According to Bordwell, who investigated various series of nitroalkanes with negative coefficients α,[71,87,88] the "nitroalkane anomaly" can be accounted for by a three-stage mechanism of the dissociation of the CH acids considered:



(7)

In the rate-limiting stage (b) the proton transfer via the C–H...B$^-$ hydrogen bond leads to the formation of a carbanion having a tetrahedral structure without a significant charge delocalisation. In the next, rapid, stage (c) the tetrahedral configuration rearranges to a planar configuration, which creates conditions in the anion for delocalisation of the charge. The influence of substituents on the rate of deprotonation of the CH acid is manifested in the slow stage involving proton transfer within the complex on passing from compound (I) to (II), while the equilibrium acidity should be determined by the effect of the substituents on the planar anion (III). There is no doubt that the structural changes in the acid influence in different ways the properties of the transition state [of stage (b)] and the anion (III). If the substituents stabilise the associated species (II) to a greater extent than the anion (III), then $\alpha > 1$; however, if the substituents have the opposite effect on the stabilities of (II) and (III), then $\alpha < 0$.

The above treatment makes it possible to throw some light onto the controversial question of the structure of the transition state in the dissociation of nitroalkanes. One must suppose that the transition state does not resemble the products, because the influences of substituents on the carbanion and on the transition state are significantly different. However, for a series of fixed nitroalkanes, $\alpha = 0.50-0.65$ and varies only slightly over a wide range of ΔpK_a as the nature of the base is varied.[79] The corresponding kinetic isotope effects are fairly large and reach a maximum near $\Delta pK_a = 0$, but in the range of ΔpK_a values greater or smaller than zero the ratios k_H/k_D vary only slightly.[87,88] The hypothesis has therefore been put forward[79] that either the transition state in the proton transfer reaction is almost symmetrical or that the quantity α and k_H/k_D are in no way related to its structure.

The above discrepancies can be eliminated when account is taken of the complex mechanism of the dissociation reaction of nitroalkanes [reaction (7)]. The quantities α and k_H/k_D should probably be referred to stage (b), the structure of the transition state of which approaches a symmetrical structure. The value of ΔpK_a for this stage is significantly smaller than that adopted in the experiment, because the latter reflects the change in the free energy throughout the entire process.[87,89]

It must be emphasised that the role of the solvation effect is significant also in the multistage mechanism,[90] because the anions of types (II) and (III) differ from one another in their capacity to form hydrogen bonds. Thus the "nitroalkane anomaly" is manifested as a consequence of the different character of the influences of the substituents on the individual stages of the dissociation process and on the solvation effects stabilising the carbanion.

In order to separate the contributions of the intramolecular electronic interactions and the solvation effects, it is necessary to study the rate of dissociation and the dissociation equilibria of CH acids in aprotic weakly polar solvents. At the present time this field of study is beginning to develop.

A detailed investigation has been made[91] of the kinetics and equilibrium in proton transfer from *p*-nitrophenylnitromethane to nitrogen-containing bases in aprotic solvents of different polarity. A parallel variation of the equilibrium and rate constants is on the whole observed for this system (with the exception of the reaction with TEA in acetonitrile): both constants increase with increase of solvent polarity and the basicity of the proton acceptor. However, no irregularities can be traced in the variation of the equilibrium or activation energy and entropy parameters. The above parallel variation is caused by combinations of the quantities $\Delta H^{\neq}$ and $\Delta S^{\neq}$, which are difficult to interpret and may be random.

Studies of the kientics of proton transfer from nitroalkane to amines in various aprotic solvents have been carried out by dynamic NMR.[92–95] In these investigations the attempts by the authors to determine separately the characteristics of the stages involving complex formation and the proton transfer proper in terms of the scheme

$$C{-}H + B \overset{(a)}{\rightleftarrows} C{-}H \cdots B \overset{(b)}{\rightleftarrows} C^- \cdots HB^+ \qquad (8)$$

are particularly interesting. Table 11 compares the results obtained. Evidently, the values of E_+ are comparable in magnitude with the heats of activation for proton transfer from *p*-nitrophenylnitromethane to amines.[91] Since both reaction (8) as a whole and stage (*b*) are thermodynamically favourable, the relations $E_+ < E_-$ holds. The anomaly is that for systems (II) and (III) the values of E_+ differ significantly for virtually equal ΔpK_a and similar values of Q. We may note that analysis of the tabulated data for system (III) leads to an unexpected result. Thus simple comparison of ΔH and E_+ shows that the energy of the transition state of the proton transfer stage is lower than the energy of the reactants. In other words the overall activation energy for the forward process in reaction (8) is negative. Under this condition, the rate of reaction should diminish with increase of temperature, which conflicts with the data of Borodin et al.[95]

Table 11. The activation energies and thermodynamic characteristics of the equilibrium in reaction (8).[92–95]

No.	CH acid	pK_a	Base	Solvent	$-\Delta H$, kcal mol^{-1}	Q, kcal mol^{-1}	E_+, kcal mol^{-1}	E_-, kcal mol^{-1}
(I)	$CH_2CH(NO_2)_2$	5.13	$NH(C_8H_{17})_2$	CCl_4	--	11	10	20
(II)	$CH_2CH(NO_2)_2$	5.13	$N(C_8H_{17})_3$	$CDCl_3$	3	12	7.9	16.9*
(III)	$(CF_3)_2CHNO_2$	5.0	$N(C_8H_{17})_3$	$CDCl_3$	6.1	12.4	4.7	11*
(IV)	$(CF_3)CH_2NO_2$	7.4	$N(C_8H_{17})_3$	$CDCl_3$	0	9	6	14

Notation: ΔH is the enthalpy of formation of the hydrogen bonds, Q the heat of reaction (8), and E_+ and E_- are the activation energies for the forward and reverse reactions of stage (b) in proton transfer.

*E_- has been determined from the formula $E_- = \Delta H - Q + E_+$.

The kinetics of proton transfer from dinitromethane to trioctylamine have been studied in aprotic solvents of different types.[94] It has been found that, with increase of the dielectric constant of the solvent on passing from cyclohexane to acetonitrile, the quantities E_+ (7.4–8.0 kcal mol^{-1}) and k_+ (27–13 s^{-1}) change insignificantly. The nature of the solvent exerts a somewhat greater influence on the heats of the equilibrium reaction, because ΔH diminishes from 4.8 to 2.2 with increasing polarity, while Q increases from 11.4 to 13 kcal mol^{-1}.

Thus, on the basis of the few date examined, one can reach the preliminary conclusion that in aprotic solvents the anomalous influence of substituents on the equilibrium and kinetic acidities of nitroalkanes diminishes but does not disappear completely.

A detailed study has been made[96,97] of the state of equilibrium and the kinetics of proton transfer from trisubstituted methanes $HC(Y)(SO_2CH_3)C_6H_4X$ (X = CH_3 or Cl; Y = COC_6H_5

or $COOC_2H_5$) to γ-collidine or TEA in methylene chloride:

$$R_3CH + N \underset{k_-}{\overset{k_+}{\rightleftarrows}} R_3C^- + HN^+ \quad . \qquad (9)$$

In the case of collidine it was found that the equilibrium constant $Kp = k_+/k_-$ and the heat Q of reaction (9) vary in parallel with the acidity of R_3C-H measured in alcohol (Table 12). In other words, the change of the solvent and the base did not alter the relative acidities of the compounds R_3C-H considered.

Table 12. Thermodynamic and kinetic characteristics of proton transfer from the trisubstituted methanes HC(Y).$(SO_2CH_3)SO_2C_6H_4X$ to γ-collidine (at 20 °C).[96]

No.	Y	X	pK_a (CH_3OH)	$\lg Kp$, (mole fraction^{-1})	$-Q$, kcal mol^{-1}	$-\Delta S$, e.u.	$\lg k_+$, (mole fraction s^{-1})	E_+, kcal mol^{-1}	$\lg k_-$, (s^{-1})	E_-, kcal mol^{-1}	$-\Delta H^*$ kcal mol^{-1}
(I)	COC_6H_5	Cl	4.77	2.8	12.4	29	3.8	5.3	1.0	17.7	3.3
(II)	COC_6H_5	CH_3	5.81	1.7	8.9	22	3.3	6.5	1.6	15.4	3.0
(III)	$CO_2C_2H_5$	Cl	5.24	1.9	7.8	18	5.7	4.4	3.8	12.2	2.6
(IV)	$CO_2C_2H_5$	CH_3	6.36	0.9	5.8	15	5.1	4.0	4.2	9.8	2.6

*ΔH is the enthalpy of the hydrogen bonds between the trisubstituted methanes and DMSO.[38]

Interesting regularities are manifested when the effects of remote (X) substituents and substituents adjoining the reaction centre (Y) are considered. Thus, for a series of isotypical compounds with the same substituent Y, the variation of X influences to a greater extent the activation energy for the protonation of the carbanion E_- than the activation energy for the deprotonation of the CH acid E_+. This is associated with the fact that the transition state of the exothermic reaction (9) resembles the initial reactant in conformity with the Hammond–Leffler postulate and its properties are determined mainly by the inductive interaction of the substituent with the reaction centre. Consequently the substituents X remote from the reaction centre should exert only a weak influence on the polarity of the C–H bond and the quantity E_+. The same substituents X are involved in the stabilisation of the carbanion via the conjugation mechanism and their influence on E_- is therefore more significant.

The replacement of the substituent Y = $COOC_2H_5$ by Y = COC_6H_5 for a constant X leads to an increase of the equilibrium acidity and the quantities Q and E_-, in conformity with the greater mesomeric effect of the benzoyl group. However, this entails an increase, albeit to a smaller extent, of E_+ and a decrease of the kinetic acidity, i.e. the Brønsted relation breaks down ($\alpha < 0$).

We interpreted the above features[108] in terms of the Bell–Evans–Polanyi potential curves (Fig.2). Fig.2 illustrates the variation of the energy of the C–H...N (family of curves I) and C^-...$H-N^+$ (family of curves II) systems with increase of the lengths of the C–H and N–H bonds respectively. In plotting the curves account was taken of the fact that (a) the substituents X in the arenesulphonyl group do not influence the form of the potential curves I but alter the position of the minimum in curves II determined by the stability of the carbanion and (b) that, for a substituent Y with a greater capacity for conjugation, a curve in family I should be steeper in the region of the transition state, since in the initial stage the energy of extension of the C–H bond involves a greater expenditure on the rearrangement of the structure.

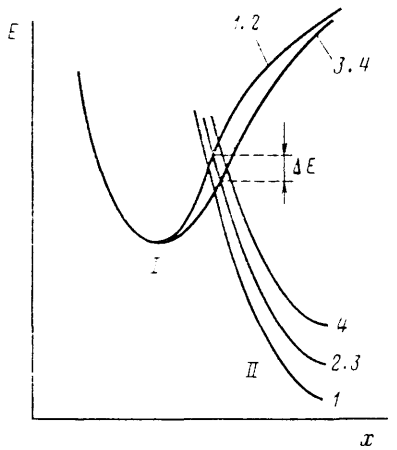


Figure 2. Cross-section through the potential energy (E) surface along the coordinate of the reaction involving proton transfer from $HC(Y)(SO_2CH_3)SO_2C_6H_4X$ to γ-collidine. Families of curves I and II refer respectively to the lengthening of the C–H and N–H bonds: 1) X = Cl, Y = COC_6H_5; 2) X = CH_3, Y = COC_6H_5; 3) X = Cl, Y = $CO_2C_2H_5$; 4) X = CH_3, Y = $CO_2C_2H_5$.

In the first place we shall compare compounds (II) and (III) which differ in the substituents X and Y but are characterised by similar values of pK_a, Kp, and Q. It follows from Fig.2 that the energies E_+ and E_- for compound (II) should be greater than for compound (III) by the same amount ΔE. This conclusion is consistent with the experimental results (Table 12).

For compounds (I) and (II) or (III) and (IV) (with Y = const.), the replacement of X = CH_3 by X = Cl leads to a decrease of E_+ (an increase of the kinetic acidity) and an increase of E_-, but, since $\Delta E_- > \Delta E_+$, this entails an increase of Kp and Q. On the other hand, on passing from Y = $COOC_2H_5$ to Y = COC_6H_5 (for X = const.), the quantities E_+ and E_- increase (the kinetic acidity falls), but, since the relation $\Delta E_- > \Delta E_+$ is maintained, Q also increases (i.e. the equilibrium acidity increases). Hence it is clear why in the pairs of compounds (I) and (II) or (III) and (IV) (i.e. with Y = const.) the equilibrium and kinetic acidities vary in parallel, while in pairs (I) and (III) or (II) and (IV) (with X = const.) their variation is antiparallel.

IX. THE ACIDITY OF UNSATURATED COMPOUNDS

The thermodynamic and kinetic acidities of hydrocarbons increase with increase of the amount of s character of the hybrid orbital forming the CH bond in the sequence $sp^3 < sp^2 < sp$. For example,

$$H_3C-CH_3\ (42) < C_6H_6\ (37) < H_2C=CH_2\ (36.5) < HC\equiv CH\ (25)$$

(the pK_a are indicated in brackets).[70] This is associated with the increase of the electronegativity of the carbon atom,

which increases the polarity of the C–H bond, and with increase of the stability of the carbanion as the energy of the orbitals of the free electron pair diminishes.

The rate of acid dissociation of ethylene and its derivatives has been scarcely investigated, since the base-catalysed proton transfer or isotope exchange reactions are accompanied by allyl rearrangements.

The hydrogen isotope exchange reactions involving benzene derivatives have been investigated.[70,98–101] It has been established that *o*-substituents accelerate the exchange (in the presence of potassium amide as the catalyst) in the sequence

$$CH_3 < H < (CH_3)_2N < C_6H_5 < CH_3O < C_6H_5O < CF_3 < F$$

and the rate of reaction is correlated with the inductive constants σ_I ($\rho = 11$). On moving away from the reaction centre, the influence of the substituents weakens and the correlation with σ_I can also break down. Thus the CF_3 group in the *m*-position accelerates the exchange to a greater extent than the fluorine atom, while the substituent CH_3O in the *p*-position diminishes the rate of exchange relative to unsubstituted benzene. These results suggest that the conjugation effect participates, apart from the inductive effect, in the stabilisation of the transition state or the carbanion. In the presence of electron-accepting substituents there is probably a possibility of the $\sigma-\pi$ interaction in the polar transition rate or in the carbanion.[98]

In the series of polysubstituted benzenes the rate of deuterium exchange increases, while the activation energy falls with increase of the number of electron-accepting substituents.[98,99] In order to understand the process mechanism, it is important to note that, when substituents in benzene or the nature of the base are varied, the results are described by the general Brønsted equation with $\alpha \approx 1$. The rates of protonation of the corresponding carbanions are independent of the structural changes ($\beta = 0$) and are similar in magnitude to the diffusion limit. Consequently, the role of conjugation in the stabilisation of the carbanion is small and the dissociation of the aryl C–H bond is not accompanied by a significant charge delocalisation and rehybridisation of the orbitals in the carbanion.[101,102]

Similar regularities are observed for acetylenic compounds. In an aqueous alcoholic medium the rate of deuterium exchange increases with increase of the inductive electron-accepting effect of the substituents in the sequence

$$HOCH_2CH_2 < HOC(CH_3)_2 < CH_3OC(CH_3)_2 < C_6H_5 < (C_2H_5O)_2CH < CH_3OCH_2.$$

Phenylacetylene remains outside the $k_+ = f(\sigma_I)$ correlation, which may be due to the resonance stabilisation of the carbanion, but the magnitude of the effect is small.[103]

The ionisation of acetylenes results in the formation of carbanions with a localised charge, since the *sp*-hybrid orbital of the free electron pair is orthogonal to the π orbitals of the triple bond and there is virtually no conjugation. The structure of the transition state resembles that of the product and the recombination of the acetylide ion proceeds at a rate which is limited by diffusion.[103–105] On the basis of the features enumerated above, substituted benzenes and acetylenes can be regarded as normal CH acids in terms of Eigen's classification.

X. THE PROTON-DONATING CAPACITY IN HYDROGEN BONDS AND CH ACIDITY

For compounds of the type $R_nX–H$ (where X are atoms of the main subgroups in Groups V–VII), it has been established reliably that, for a fixed X and variable substituents R, the strength of the hydrogen bonds X–H...B and the equilibrium acidity of the compound $R_nX–H$ vary in parallel. The same relation between the proton-donating capacity and acidity has been observed in a series of compounds R_nXH, provided that X represents atoms of elements of a single Period (X = O, N, or F). On the other hand, in the series of structurally isotypical compounds of elements of one Group but different Periods (X = N, P, As or O, S, Se) the variation of the proton-donating capacity and equilibrium acidity is antiparallel. However, for compounds with X–H groups the decrease of the proton-donating capacity is as a rule accompanied by a fall of kinetic acidity.[4]

For CH acids, virtually no comparisons have been made of the proton-donating capacity in hydrogen bonds and the thermodynamic and kinetic acidities. It has only been suggested[2] that the relatively low rates of ionisation of CH acids are caused by the weak capacity of the CH groups for the formation of hydrogen bonds. The data available at present make it possible to consider the relation between the proton-donating capacity and the CH acidity in greater detail.

It has been established[20,106] that the strength of the C–H...B hydrogen bonds between haloforms and electron donors of different types diminishes in the sequence

$$Cl_3CH > Cl_2BrCH > Br_3CH > F_3CH > I_3CH$$

and, with the exception of fluoroform, is correlated with the electronegativity of the halogens. The kinetic acidity diminishes on passing from iodoform to fluoroform:

$$I_3CH > Br_3CH > Cl_2BrCH > Cl_3CH > F_3CH \text{ (Refs.57–58).}$$

The replacement of one of the halogen atoms by a more complex electron-accepting substituent does not alter the above sequences.[34,80] Thus the variation of the proton-donating capacity in the formation of hydrogen bonds and of the kinetic acidity of compounds containing halogen atoms is antiparallel. If account is taken of the fact that in the series of compounds considered the variation of the kinetic and equilibrium acidities obeys the Brønsted equation, it becomes clear that the variation of the proton-donating capacity and of the thermodynamic acidity is antiparallel.

The above features are due to the fact that the proton-donating capacity in hydrogen bonds is determined primarily by the polarity of the CH bonds, which depends in its turn on the electronegativity of the halogen. Fluoroform, in the molecule of which the positive charge on the hydrogen atom is minimal because the $+M$ effect is a maximum for fluorine, is an exception. On the other hand, the acidity of haloforms is determined mainly by the stability of the carbanion, determined by conjugation involving the *d* orbitals and the $+M$ effect.[1]

The CF_3 group, interacting with the reaction centre of the acid and the anion predominantly via the inductive mechanism, has a parallel influence on the proton-donating capacity and the kinetic acidity. Thus the replacement of the chlorine atoms by the CF_3 groups increases the strength of the hydrogen bonds with DMSO from 1.6 kcal mol^{-1} for chloroform to 5.6 kcal mol^{-1} for $(CF_3)_3CH$ [28,29] and accelerates the deuterium–hydrogen exchange [the constants k_+ for the compounds $(CF_3)_2C_6H_5CH$, CF_3CHCl_2, $(CF_3)_2CHCl$, and $(CF_3)_3CH$ are in the ratios 1 : 2.3 : 651 : 4290].[60]

The substitution of the CF_3 group by the strong electron-accepting substituents NO_2 and CN strengthens the acidity but reduces the proton-donating capacity (Table 13). It is of interest to note that, for compounds (II) and (IV), which have similar equilibrium acidities, the activation energies for the abstraction of a proton are correlated with the strength of the hydrogen bonds. Presumably in the systems discussed the structure of the transition state is more like that

of the initial hydrogen-bonded molecular complexes than that of close ion pairs. This probably constitutes the cause of the parallel influence of substituents on the proton-donating capacity and the kinetic acidity.

Table 13. The enthalpies of the hydrogen bonds with DMSO and the activation energies for proton transfer from CH acids to amines.[1,29,93,94]

No.	CH acid	pK_a	$-\Delta H$, kcal mol^{-1}	E_+, kcal mol^{-1}
(I)	$(CF_3)_3CH$	7.0	5.63	—
(II)	$(CF_3)_2CHNO_2$	5.0	4.82	4.7
(III)	$(CF_3)_2CHCN$	0	4.75	—
(IV)	$CH_3CH(NO_2)_2$	5.2	2.23	7.9

In the series of dinitriles, parallel changes in the formation constants of the hydrogen bond and the equilibrium as well as kinetic acidities are observed. The introduction of a bromine atom into the malononitrile molecule increases the acidity and proton-donating capacity, while the introduction of the phenyl group diminishes these quantities (Table 14). The nature of CN substituents is such that they influence the reaction centres of the acids and anion via a single mechanism—the inductive mechanism (see Section VII). The introduction of these groups therefore leads to a parallel variation of the polarity of the C–H bonds and of the stability of the carbanions.

Table 14. The formation constants of the hydrogen bonds with HMPA and dimethylformamide (DMF) (in carbon tetrachloride) and the relative rate constants for the ionisation (in H_2O) of a series of dinitriles.[34]

CH Acids	K, litre mol^{-1} (HMPA)	K, litre mol^{-1} (DMF)	pK_a	k_+^{**}
$CHBr(CN)_2$	205	—	7.8	10^8
$CH_2(CN)_2$	60	11.4	11.1	10^6
$C_6H_5CH(CN)_2$	—	5.28	13.1*	1*

*The values of pK_a and k_+ are quoted for the compound $O_2NC_6H_4CH(CN)_2$.[63]
**The constant k_+ has been estimated from the data of Hibbert and co-workers.[62,63]

In the series of trisubstituted methanes of the type $HC(Y)(SO_2CH_3)SO_2C_6H_4X$ there is no general relation between the thermodynamic or kinetic acidity and the strength of the hydrogen bonds with electron donors (Table 12). A change in the nature of the substituent Y adjoining the reaction centre induces a change in the proton-donating capacity, which is in parallel with the change in the equilibrium acidity but is antiparallel in relation to the kinetic acidity. Within a series of isotypical compounds (for a fixed Y), the influence of a remote substituent X on the proton-donating capacity agrees better with its influence on the kinetic acidity than on the equilibrium acidity. These relations are caused by the initial reactant-like structure of the transition state in the dissociation reactions of the CH acids considered, whose energy, like the polarity of the C–H bonds, is determined mainly by the inductive influence of the substituents.

The proton-donating capacity and acidity of substituted bezenes increase after the introduction of electron-accepting substituents. Thus an increase of the number of chlorine atoms from 3 to 5 leads to an increase of the constant for association with HMPA [34] and to a decrease of pK_a from 34 to 30.[107] Since $\alpha = 1$ and $\beta = 0$ ($k_- = \text{const.}$) for substituted benzenes and K_a is therefore proportional to k_+, one may expect a correlation of the proton-donating capacity not only with the thermodynamic acidity but also with the kinetic acidity.

The character of the variation of the proton-donating capacity of the acetylenic compounds $RC{\equiv}CH$ can be inferred from the chemical shift of the signal due to the CH protons in associated species with pyridine,[48] which increases in the following sequence of substituents R:

$$HO(CH_2)_2<HOC(CH_3)_2<CH_3OC(CH_3)_2<C_6H_5<(C_2H_5O)_2CH.$$

The deuterium exchange rate constants increase in the same sequence.[103] Evidently, the inductive influence of R determines the proton-donating capacity and the kinetic or equilibrium acidity of the acetylenic compound, since the *sp*-hybrid orbital of the free electron pair in the acetylide ion is orthogonal with respect to the π orbitals and there are no effects of conjugation with the substituent. This applies also to the transition state whose structure resembles that of the product.[105]

Thus among CH acids there are a series of compounds differing in the character of the relations between the proton-donating capacity in hydrogen bonds and the acidity. These differences are caused primarly by the fact that the influence of substituents on the properties of CH acids discussed is exerted via mechanisms of different nature. Thus the proton-donating capacity of CH groups depends on their polarity and is therefore determined mainly by the inductive effect of the substituents. The equilibrium and kinetic acidities depend both on the inductive and mesomeric effects of the substituents. The predominance of particular mechanisms of the substituent influence is associated both with the structure of the acid and the carbanion and with the structure of the transition state.

Since the C–H...B hydrogen bonds are located on the coordinate of the deprotonation reaction of CH acids, we shall attempt in the first place to determine the relations between the proton-donating capacity in hydrogen bonds and the kinetic acidity. Analysis of the results presented above suggest that a parallel variation of ΔH and k_+ or E_+ should be observed in a series of acids for which the kinetic and equilibrium acidities are determined by the polar effects of the substituents which are virtually incapable of mesomeric interaction; either the transition state in the transfer of the CH proton resembles the initial reactant and the substituents of any type influence the kinetic acidity mainly via the inductive mechanism or the transition state of the reaction has a structure close to that of the carbanion, but the conditions for conjugation between the free electron pair and the substituents are lacking for steric reasons.

Evidently, when the Brønsted relation holds in the series of CH acids satisfying the conditions indicated, then the proton-donating capacity should be correlated not only with the kinetic acidity but also with the thermodynamic acidity.

The correlation between ΔH and $k_+(E_+)$ breaks down if a transition state, to the stabilisation of which the effects of the conjugation between the reaction centre and the substituents make a significant contribution, corresponds to the

deprotonation of the CH acids. Presumably in reaction series of this kind the form of the potential curve corresponding to the extension of the C–H bond depends on the nature of the substituent.

In comparing the properties of the C–H...B bonds and the CH acidity, we did not consider the questions of the properties of the $C^-...HB^+$ hydrogen bonds. In aprotic solvents these bonds determine in many respects the stability of the ion pair, while in protic solvents (SH) bonds of the type $C^-...HS$ play a significant role in solvation effects. Thus the problem arises of the relation between the electron-donating (proton-accepting) capacity of the carbanions in hydrogen bonds and their kinetic stability (basicity). However, there are so far virtually no literature data necessary for such a comparison. Experimental and theoretical study of hydrogen bonds involving carbanions is therefore urgently required.

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Pisarzhevskii Institute of
Physical Chemistry, Academy of
Sciences of the Ukrainian SSR,
Kiev

Translated from *Uspekhi Khimii*, **54**, 2009-2023 (1984) U.D.C. 541.14

The Photochemistry of Metallocenes

N.S.Kochetkova (deceased), M.-G.A.Shvekhgeimer, and L.V.Balabanova

The problems of the photochemistry of the dicyclopentadienyl derivatives of Group VIII metals are considered. Examples of the use of the photochemical reactions of metallocenes for the preparation of light-sensitive materials, inhibitors of the photoageing of polymers, catalysts of the photodecomposition of polymers, etc are presented.
The bibliography includes 125 references.

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I. INTRODUCTION

The photochemistry of metallocenes (dicyclopentadienylmetals) has been developing vigorously mainly during recent years. The planned investigation of the photochemistry of ferrocene and its derivatives as well as ruthenocene and osmocene was begun about 10 years ago in a number of countries. Data obtained up to 1977 are surveyed in a monograph[1] published in 1979; later reviews devoted to the photochemistry of metallocenes are not available in the literature. The aim of the present review is to survey the literature data on the photochemistry of metallocenes published mainly during the last 10–12 years. Attention has been concentrated on the photochemistry of the cyclopentadienyl derivatives of Group VIII metals, since these are most readily available and are of interest from the practical point of view.

II. FERROCENE AND ITS DERIVATIVES

We shall consider the current ideas about the electronic configuration of the ground and certain excited states of ferrocene and ferrocenium salts. The details of the electronic configuration are still the subject of discussion and the results of theoretical calculations are not always consistent with the experimental data obtained.[2-12]

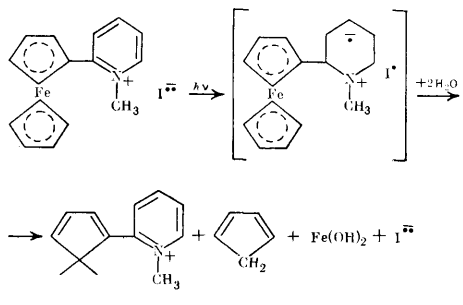
The distribution of the energy levels of ferrocene in the ground state has been investigated[13] on the basis of the EPR and photoelectron spectra (Fig. 1*a*). On photoexcitation, the ferrocene molecule passes from the $^1A_{1g}$ singlet state (or possibly from the $^1E_{2g}$ state) to the excited $^3E^*_{1g}$ triplet state (Fig. 1*b*). Oxidation results in the formation of the ferrocenium ion Fc^+ (doublet $^2A_{1g}$ state) (Fig. 1*c*). A similar estimate of the energies of the e_{1g} and a_{1g} levels of the ferrocenium ion constitutes the basis of the scheme presented in the monograph of Jeoffroy and Wrighton,[1] where these values are believed to be virtually identical.

The difficulties arising in the interpretation of the bands in the electronic spectra of ferrocene are indicated in another monograph.[14] For the interpretation of the bands in the electronic absorption spectra of ferrocene and other metallocenes, reliable experimental data are therefore required over the widest possible spectral range. To achieve reliability, studies by different and independent methods are essential.

The view that the ferrocene system is extremely resistant to various types of radiation existed for a long time in the literature.[15] For example, it has been stated that ferrocene is stable under irradiation[17] and also that the Szillard–Chalmers reaction has been carried out with ferrocene[16] in which irradiation of ferrocene with fast neutrons results in the formation of a metallocene containing ^{59}Fe; it is remarkable that this process proceeds without significant decomposition of the ferrocene system. The resistance of ferrocene to the action of light in solutions in decalin, cyclohexane, and alcohols has also been noted.[18]

However, subsequent studies showed that ferrocene and its derivatives are capable of undergoing photodecomposition reactions. The first studies on the photodecomposition of ferrocene derivatives containing electron-accepting substituents linked directly to the cyclopentadienyl ring[19,20] and also separated from it by vinyl[21] of phenylene[22,23] groups were carried out by Nesmeyanov, Sazonova, and coworkers. The decomposition of α-ferrocenyl-*N*-methylpyridinium salts has been studied in greatest detail[24-27] and the photodecomposition mechanism presented in Scheme 1 has been proposed for them.

Scheme 1



According to this mechanism, the transfer of an electron from the anion to the pyridinium system results in the formation of a relatively unstable intermediate species which decomposes under the influence of irradiation giving rise to 2-cyclopentadienyl-1-methylpyridinium, cyclopentadiene, and iron hydroxide.

Traverso and coworkers[28–33] investigated the processes occurring in the photolysis of ferrocene and its derivatives in different solvents. A detailed study of the photodecomposition of ferrocene in the presence of CCl_4 and $CHCl_3$ [28] showed that the process proceeds in a more complex manner than had been supposed by Brand and Sneddon.[29] It was found that the quantum yield of the photodecomposition is much greater than unity and depends appreciably on the ferrocene concentration in solution. The abstraction of an electron under the influence of radiation can be accompanied by a secondary chemical interaction of ferrocene with the reactive radicals $CCl_3^{\cdot}$ and $CHCl_2^{\cdot}$. Traverso and Scandola[28] observed bands in the absorption spectra of the reaction products which had been shown earlier by Nesmeyanov et al.[6] to correspond to charge transfer from the metal to the cyclopentadienyl ring. This constitutes an important confirmation of the proposed mechanism. If ferrocene is in an excited state, then the electron initially passes from the orbital associated mainly with the metal to one associated mainly with the ligand and is then abstracted. The absence of the products of the photochemical oxidation of ferrocene itself in the case of spectroscopically inactive solvents cannot serve as an argument in support of the mechanism involving charge transfer to the solvent molecule according to Traverso and Scandola,[28] because the abstraction of an electron in these solvents by radiation may become reversible.

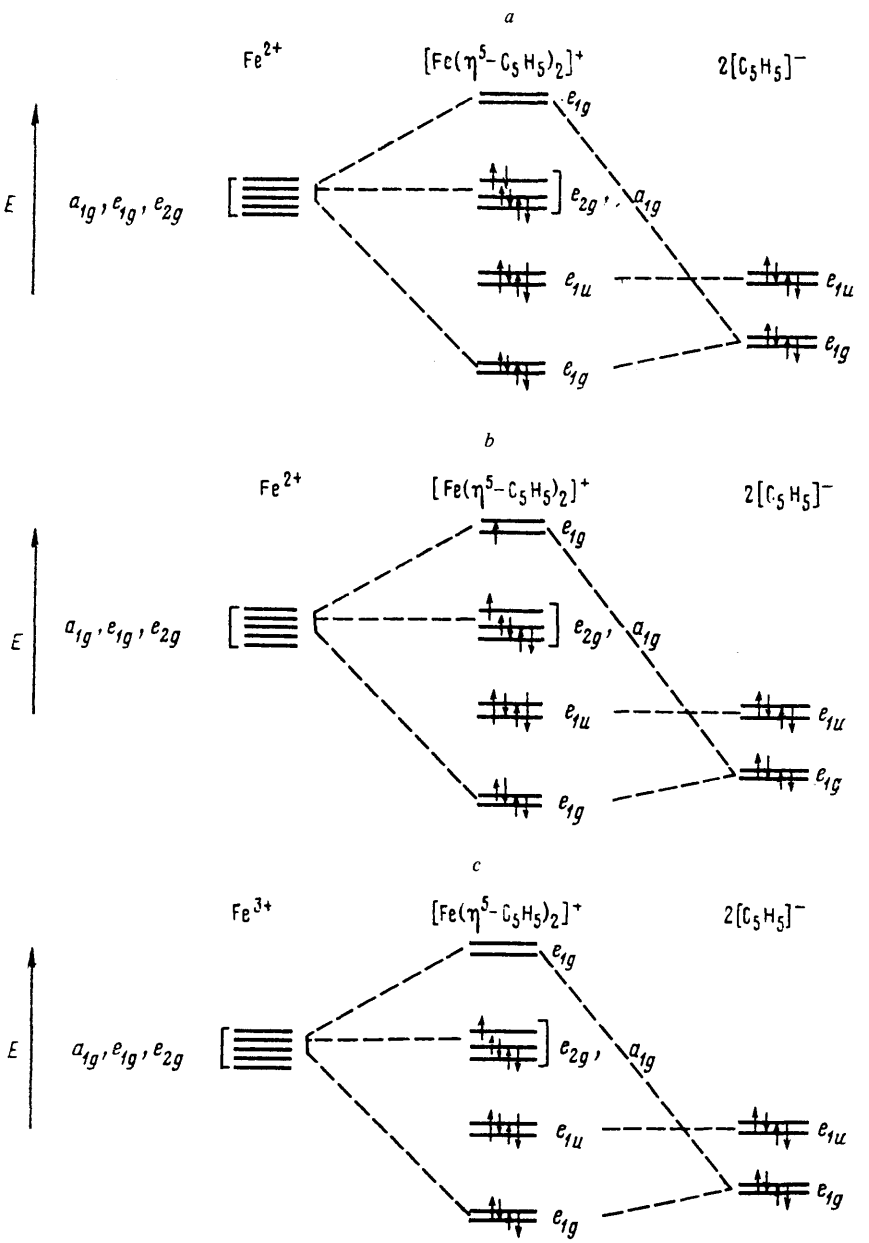


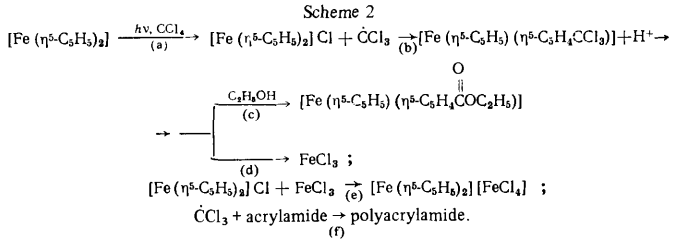
Figure. Energy level schemes for the ground (*a*) and excited (*b*) states of ferrocene (Fc^*) and the state of the ferrocenium ion (Fc^+) (*c*).

The photochemical behaviour of benzoylferrocene in solution in methanol, absolute ethanol, or 1-propanol under irradiation by monochromatic light in the range 313–472 nm has been investigated by Traverso et al.[30] Benzoylferrocene passes to an excited state and, after electron transfer, is oxidised to the corresponding benzoylferrocenium cation; the presence of a hydrogen bond between benzoylferrocene and the hydroxylated solvent facilitates this process. The authors[30] suggested that the substitution product is $RC_5H_4FeC_5H_5$, but were unable to identify it; it was isolated subsequently.[34–38]

The photolysis of ferrocene in alcohol in the presence of a mixture of halogenohydrocarbons has been studied.[34–38] The photolysis of ferrocene in ethanol in the presence of CCl_4 leads to the ethyl ester of ferrocenecarboxylic acid. When the photolysis is carried out in other alcohols, the reaction hardly occurs. Formylferrocene and ferrocenylmethanol are formed respectively in low yields in the presence of $CHCl_3$ and CH_2Cl_2.

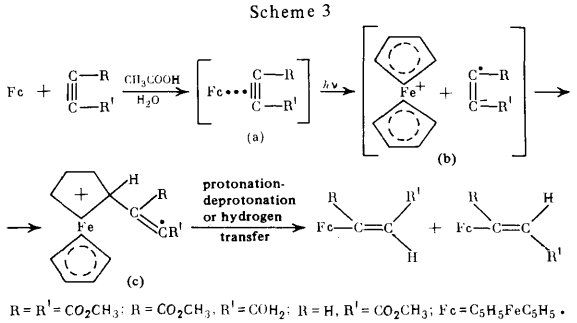
In the photolysis of ferrocene in the presence of halogenohydrocarbons initially all this results in the formation of ferrocenium halide and the radical of the corresponding halogenohydrocarbon (Scheme 2*a*). The subsequent course of the reaction can be different. In the presence of an alcohol, ferrocene substitution products are formed and the reaction proceeds with formation of a new C – C bond; in the presence of acrylamide, either the latter polymerises or ferrocenium salts are formed (see Scheme 2, stages *e* and *f*).[37]

Scheme 2



It has been established[38] that, when a mixture of ferrocene and dimethyl acetylenedicarboxylate is irradiated with ultraviolet light in an aqueous acetic acid solution, a mixture of dimethyl ferrocenylmaleate and dimethyl ferrocenylfumarate is formed. If acetylenedicarboxylic acid, methyl 3-carbamoylpropiolate, acetylenedicarboxylic acid dinitrile, or methyl propiolate are used instead of dimethyl acetylenedicarboxylate, the corresponding ferrocene derivatives are formed. It is noteworthy that acetylene derivatives containing electron-accepting substituents enter into the reaction in this case; it is believed[37,38] that the reaction mechanism involves the initial stage in which a charge-transfer complex is formed and then decomposes into the ferrocenium cation and a radical-anion (Scheme 3*b*); this is followed by the formation of the ferrocenium radical-cation (Scheme 3*c*), which is converted into methyl β-ferrocenylacrylate (for R = H) or into a mixture of derivatives of maleic and fumaric acids (for R = $COOCH_3$).[38]

Scheme 3



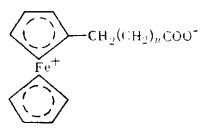
R = R' = CO_2CH_3; R = CO_2CH_3, R' = COH_2; R = H, R' = CO_2CH_3; Fc = $C_5H_5FeC_5H_5$.

When acetone, acetonitrile, ethyl acetate, or methanol were used as solvents, the yield of substitution products was appreciably lower.

The use of nitrous oxide in the study of the photochemistry of ferrocene made it possible to follow the course of the electron transfer process and to estimate the quantum yield of the overall reaction from the amount of gaseous nitrogen evolved.[39–49] Apart from ferrocene,[39,40] the photochemistry of methyl-, 1,1'-dimethylphenyl-, and acetyl-ferrocenes[41,42] has been studied by this method. Electrochemical and photochemical data have demonstrated the similarity of the influence of the substituent on the abstraction of an electron from the ground and photoexcited states; the quantum yield was appreciably less than unity under these conditions.

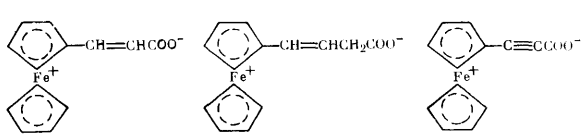
Nitrous oxide has also been used in the study of the photochemical behaviour of ferrocenylalkane- and ferrocenylalkenecarboxylic acids[42–46] on irradiation with light at a wavelength of 254 nm. It was shown that the quantum yields of the processes vary linearly with the N_2O concentration. The authors suggest that the low quantum yield can be accounted for by the fact that the photoinitiated stage is not the only one occurring on absorption of light and is accompanied also by a dark reaction. Thus direct electron transfer from the ferrocenyl component of the molecule to N_2O is believed by the authors to be more probable than electron transfer to the hydroxylated solvent. This is demonstrated by the presence in the irradiated specimens of cyclopentadiene, detected by means of gas–liquid chromatography.

Subsequently the same workers[45–47] showed that on photoirradiation the electron can readily pass from the excited triplet state of the ferrocene molecule to an acceptor of the type N_2O; the lifetime of the excited triplet state is then extremely short, amounting to 1 μs. In an alkaline medium the product of such transfer exists in the form of a stable dipolar ion:



It was found that the electronic absorption spectrum of such a dipolar ion resembles that of ferrocenium salts. Chemical reduction led to the recovery of the initial acid. Thus the process proceeds without the decomposition of the ferrocene system.

In the same series of investigations[41,42] studies were made not only of the reactions of β-ferrocenylpropionic acid in aqueous alkaline media (borate buffer at pH 9–10) but also chain growth was achieved and the resulting γ-ferrocenylbutyric and δ-ferrocenylvaleric acids were studied in order to check that intramolecular electron transfer occurs on photoexcitation.[44] However, a chain of four–five carbon atoms with free rotation about a single bond can at some instant occupy a position such that the carboxylate anion is fairly close to the iron atom. The authors therefore subsequently investigated the photolysis of ferrocenylalkene- and ferrocenylalkyne-carboxylic acids in the molecules of which the double or triple bond rules out the possibility of the rotation of the chain and the approach of the "COO" group to the iron atom. The existence of the following dipolar ions was demonstrated experimentally:[45,46]



The dipolar ions are formed as a result of the irradiation of the corresponding acids with light at a wavelength of 240 nm in an aqueous borate buffer in the presence of N_2O. The author suggests that three processes take place under these conditions:[46] (1) photoexcitation of the molecule in the ground state to a short-lived triplet state (a first-order reaction); (2) reaction with N_2O, giving rise to the dipolar ion and N_2; (3) quenching of the excitation induced by the addition of alcohols.

Thus in solvating solvents and also in the presence of electron acceptors, both in solution and incorporated in the molecule of the test substance, ferrocene and its derivatives undergo complex photolytic and oxidation processes, which in some instances are accompanied either by substitution in the cyclopentadienyl ring with formation of new C–C bonds or by the decomposition of the ferrocene system.

When ferrocene and its derivatives are exposed to visible light in alcohol in the presence of oxygen, no less complex processes occur. However, they are not accompanied by the decomposition of ferrocene, its homologues and ferrocenium salts. The auto-oscillatory photochemical processes occurring in alcoholic solutions of ferrocene, octamethylferrocene, and the corresponding ferrocenium hexafluorophosphates on irradiation with visible light from a 500 W incandescent lamp have been described for the first time in a number of communications.[50-54] A periodic increase and decrease of the intensity of the bands in the absorption spectra of solutions of this substance were observed under these conditions. It was established that the period of the oscillation of the intensity increases with increase of the concentration of the solution, decreases with increasing temperature, and depends on the concentration of oxygen in the system. There is an oxygen concentration at which the period of the oscillations is a minimum.[52] A mechanism has been proposed for this multistage process with participation of alcohol and oxygen, in which ferrocene plays the role of the photosensitiser.[54]

The reaction between alcohols and alkyl isocyanates, catalysed by the light-sensitive ferrocene–$FeCl_3$ system, has been examined by Wilfutte-Steinert.[55] The kinetics of the interaction of t-butyl isocyanate with methanol in the presence of ferrocene at 25 °C have been investigated by infrared and ultraviolet spectroscopy in solution in the CCl_4–CH_2Cl_2 mixture under illumination with monochromatic light at 365 nm. After an induction period of 15 min, the rate of decomposition of t-butyl isocyanate obeys a zero-order kinetic equation; this is associated with the absorption of light by the $FeCl_4^-$ ions which are formed on irradiation of ferrocene in CCl_4 and absorb 99% of the incident light after 30 min of reaction. An ionic-chain mechanism with radical initiation has been proposed for the reaction. The initiation stages

$$Fe^{3+} + Cl^- \xrightarrow{h\nu} Fe^{2+} + \dot{C}l$$

$$\dot{C}l + RNCO \rightarrow RNCO^+ + Cl^-,$$

are accompanied by chain propagation reactions:

$$RNCO^+ + R'OH \rightarrow \overset{+}{R}NHCOOR' \rightarrow RNHCOOR' + RNCO^+.$$

The quantum yield of the reaction is 0.3. Another possible mechanism has been proposed for the chain propagation stage:

$$RNCO^+ + Fe^{2+} \rightarrow RNCO + Fe^{3+}.$$

The consumption of Fe^{3+} is compensated by the oxidation of Fe^{2+} by the ferrocenium cation.

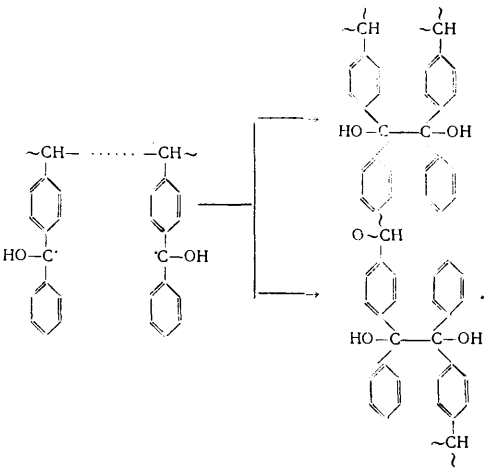
Certain ferrocene derivatives, for example, ketones, behave specifically under illumination. It is known that aromatic ketones are readily converted into pinacones on irradiation. However, this type of reaction has not been observed for ketones of the ferrocene series: on irradiation in the presence of proton or electron donors, they give rise to the corresponding ferrocene alcohols:

$$Fc{-}COR \xrightarrow{h\nu} Fc{-}\overset{OH}{\overset{|}{C}}HR,$$

where R = H, CH_3, or C_6H_5.[56] In propanol this reaction proceeds with an insignificant quantum yield (~0.002). It has been stated[18] that the photodecomposition of acetylferrocene is hardly observed in isopropyl alcohol. However, when the reaction is carried out in the presence of reductants [$(C_4H_9)_3SnH$ and $(C_6H_5)_3SnH$], the photochemical reduction of acetylferrocene leads to the corresponding alcohols with a quantum yield higher by an order of magnitude (~0.02).[56] The authors believe that in the excited state the oxygen atom of acetylferrocene can have a distinctly radical character and that photoexcitation is due to the $d \cdot d$ transitions at the central iron atom and not the $n \cdot \pi^*$ transitions in the ligand. Consequently the reduction of ketones derived from ferrocene is due to the low energy of the excited state.

Sandez et al.,[57] who investigated the chemical behaviour of vinyl-benzophenone (VBP) polymers and VBP–vinylferrocene copolymers on irradiation, adhere to similar ideas. It has been found that the morphology of the polymer chains in the VBP polymer changes significantly as a consequence of the photochemical oxidation and intramolecular processes (cyclic and cross-linked structures appear–see Scheme 4).

Scheme 4



The polymer then becomes brittle and acquires some undesirable properties. On the other hand, irradiation of VBP–vinylferrocene copolymers in the presence of isopropyl alcohol does not entail significant changes in their physicochemical properties. These data permit the conclusion that ferrocene derivatives inhibit the photoageing processes in polymers.

A new absorption band has been observed in the electronic absorption spectrum of a solution of ferrocene in CCl_4[58] and was assigned to charge transfer to the solvent. The irradiation of this solution results in the formation of ferrocenium tetrachloroferrate $[C_5H_5FeC_5H_5]^+FeCl_4^-$.

The photochemical reactions of charge-transfer complexes (CTC) based on ferrocene or its derivatives and polyhalogenohydrocarbons (CBr_4) have been studied in detail recently.[60-64] The investigation of the spectroscopic characteristics of the CTC formed on interaction of CBr_4 with ferrocene or its derivatives showed that the ferrocene molecule forms a complex with three CBr_4 molecules.[59] The introduction of substituents into the ferrocene molecule alters the composition of

the CTC produced. Monosubstituted ferrocene derivatives form a complex incorporating two CBr_4 molecules. The introduction of substituents into both cyclopentadienyl rings alters the composition of the complex to one corresponding to the 1 : 1 ratio.

Investigation of the influence of the substituent on the position of the absorption band maximum in the electronic spectra of monosubstituted and heteroannular disubstituted ferrocene derivatives with electron-donating and electron-accepting substituents showed[4,6,11] that the shift of the long-wavelength band maximum at 440–560 nm resulting from the introduction of substituents into ferrocene is not great (3–15 nm), but it depends appreciably on the electronic character of the substituent. The 440 nm band undergoes a small hypsochromic shift in the case of electron-donating substituents and a bathochromic shift in the case of electron-accepting substituents.[6]

On the other hand, when CTC are formed, the influence of the substituents on the spectrum is much greater: the band shift amounts to 50–100 nm. The introduction of electron-accepting substituents into the ferrocene molecule causes a hypsochromic shift of the CTC band maximum, while the introduction of electron-donating (alkyl) groups results in a bathochromic shift. The greatest displacement of the CTC band maximum is observed in the electronic spectrum of the symmetrical octamethylferrocene;[10] λ_{max} for the ferrocene–CBr_4 CTC differs from λ_{max} for octamethylferrocene–CBr_4 CTC by 112 nm. All these factors permit the selection, by varying the chemical nature of the substituent in one or both cyclopentadienyl rings of ferrocene, of systems whose photosensitivities lie within a wide range in the spectrum.

The formation of CTC by ferrocene and its derivatives with tetranitromethane in methanol has been demonstrated.[64,65] The authors of both studies postulate the formation of a ferrocene-tetranitromethane CTC in accordance with the scheme

$$C_5H_5FeC_5H_5 + C(NO_2)_4 \rightarrow C_5H_5FeC_5H_5 \cdot NO_2 + C(NO_2)_3^{\cdot}.$$

It has been shown[65] that ferrocene derivatives such as vinyl-, acetyl-, 1,1'-dimethyl-, 1,1'-diethyl-, and benzoyl-ferrocenes also form CTC with nitromethane.

The photochemical reaction between ferrocene and iodine in water has been studied by flash photolysis.[66,67] It has been established that the photodissociation of the iodine molecule (I_2) is followed by the two-stage formation of ferrocenium tri-iodide:

$$C_5H_5FeC_5H_5 + I \rightarrow C_5H_5FeC_5H_5^+ I^-,$$

$$C_5H_5FeC_5H_5^+ I^- \xrightarrow{I_2} C_5H_5FeC_5H_5^+ I_3^-,$$

which proceeds much more vigorously than the recombination of iodine atoms.

The photoinitiated interaction of ferrocene with iodine in benzene has been studied by flash photolysis[68] and it has been shown that the reaction proceeds as follows:

(1) the iodine molecule initially undergoes photodissociation into atoms and an iodine-benzene CTC is formed:

$$I + C_6H_6 \rightarrow C_6H_6 \cdot I;$$

(2) this is followed by the oxidation of ferrocene with atomic iodine (or the oxidation of the iodine–benzene CTC) with formation of the ferrocenium iodide ion pair:

$$I \cdot C_6H_6 \rightarrow C_5H_5FeC_5H_5^+ I^- + C_6H_6;$$

(3) finally ferrocenium iodide reacts with another iodine molecule to form ferrocenium tri-iodide:

$$C_5H_5FeC_5H_5^+ I^- + I_2 \rightarrow C_5H_5FeC_5H_5^+ I_3^-.$$

It has been established that the last two processes have similar rates.

1. Ferrocenium Salts

Hitherto the photodecomposition of ferrocenium salts has not been studied in detail. It has been reported[58] that the photolysis of ferrocenium tetrachloroferrate in a $CCl_4 + C_2H_5OH$ mixture results in the formation of only ferrocene and a small amount of hexachloroethane owing to the recombination of the trichloromethyl radicals produced on irradiation.

The photolysis of ferrocenium chloride has been investigated[69] in aqueous acid $H_2O|CH_3OH|HCl$ media and the formation of ferrocene with a quantum yield of 0.029 was observed. In more dilute acid solutions, decomposition to inorganic iron (II) salts takes place

III. RUTHENOCENE AND OSMOCENE

In contrast to ferrocene, an emission spectrum has been observed for ruthenocene which is fairly well resolved at a low temperature. The presence in this spectrum of the $d \cdot d$ transition band at 510 nm and the ability of ruthenocene to quench excited triplet states are attributed to the presence of a triplet level in the energy spectrum of its excited molecule.[3]

Independent studies by two groups of workers[2,70] showed that the photochemical behaviour of ruthenocene has much in common with that of ferrocene. On irradiation with light at a wavelength of 254 nm in cyclohexane, ruthenocene is inert, while in the presence of halogenohydrocarbons photolysis takes place, as for ferrocene, with the appearance of a charge-transfer band and oxidation to the ruthenocenium cation.

Thus, analogously to the photolysis of ferrocene, the process proceeds in accordance with the scheme

$$C_5H_5RuC_5H_5 + RCl \xrightarrow{h\nu} [C_5H_5RuC_5H_5]^+ Cl^- + R^{\cdot}.$$

Further irradiation leads to the appearance of turbidity in the solution and the precipitation of ruthenocenium tetrachlororuthenate. When the photolysis is carried out in the presence of acrylamide, the latter polymerises, which indicates indirectly the presence of radicals in the system. The quantum yield is high and, according to the data of different workers, assumes values ranging from 0.6 to 1. It may be that part of the ruthenocene is oxidised by a secondary reaction to ruthenocenium tetrachlororuthenate.

In later investigations, Traverso and coworkers[43] studied the photolysis of ruthenocene, benzoylruthenocene, and osmocene in the presence of tetracyanoethylene (TCE). The formation of complexes between the metallocene and TCE was then established by ultraviolet spectroscopy. Charge-transfer bands were observed at the boundary between the visible and infrared regions (720–830 nm). The authors discovered a linear relation between the position of the charge-transfer band maximum for the metallocene–TCE complexes in the electronic absorption spectrum in cyclohexane and the oxidation potential $E_{1/4}$; on this basis, they concluded that the TCE molecule is coordinated to the metal atom. In this connection the authors suggest that the difference between the energies of the two maxima on the absorption curve of the charge-transfer bands is associated with the difference between the energies of the two highest occupied orbitals of the metal. The difference between the energies of the $a_{1g}(d)$ and $e_{2g}(d)$ orbitals is 1452 cm^{-1} and corresponds to the difference between the ionisation energies obtained for the He-photoelectron spectra of ruthenocene and osmocene.[71] This result also constitutes an argument in support of the direct involvement of the metal atom in the bond with TCE, i.e. it is probable that the electron pair participating in the formation of the CTC is localised mainly at the metal.

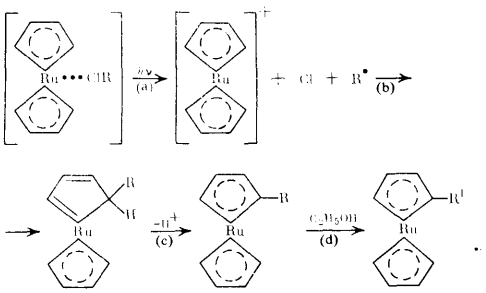
The photolysis of the CTC involves the following processes:

$$C_5H_5MC_5H_5 \cdot TCE \xrightarrow{h\nu} [C_5H_5MC_5H_5 \cdot TCE]^* \rightarrow \begin{cases} \longrightarrow C_5H_5MC_5H_5 + TCE \\ \longrightarrow [C_5H_5MC_5H_5]^+ + TCE^{\cdot-}; \end{cases}$$

M=Ru, Os .

The quantum yield in the formation of TCE is 0.75–0.68 and is independent of the wavelength of the incident light.

Sujimori et al.[72] carried out the photochemical ethoxymethylation, formylation, and ethoxycarbonylation of ruthenocene on irradiation of the latter in alcohol in the presence of the corresponding halogenohydrocarbons; the yields amounted to 10–20%. In the case of $CHCl_3$, formylruthenocene is formed in 39–57% yield on irradiation from a light source fitted with a pyrex glass filter. The authors presented the following process mechanism:



The reaction proceeds analogously to that described above for ferrocene.

Thus the photochemistry of ruthenocene has much in common with that of ferrocene; the reactions of both metallocenes take place via two pathways: (1) the oxidation of the metallocene and (2) further reactions with formation of new C–C bonds.

IV. COBALTOCENE AND NICKELOCENE

When cobaltocene is irradiated with light at a wavelength of 254 nm, it is oxidised and the cobaltocenium cation, stable under the irradiation conditions, is formed readily.[73] This is confirmed by the possibility of the quantitative spectrophotometric determination[73] of the cobaltocenium cation in aqueous solution over a wide pH range.

Aqueous solutions of cobaltocenium salts exhibit not only light stability but also radiation stability.[74,75] It is noteworthy that the character of the ultraviolet spectra of the cobaltocenium cation remains unchanged also after prolonged heating of its aqueous solutions at 200 °C.[75] Thus the photochemical behaviour of cobaltocene differs appreciably from that of the other metallocenes.

In contrast to cobaltocene, when nickelocene is irradiated with light at a wavelength of 254 nm, a polymer is formed and the quantum yield is 0.007. The primary oxidation product (nickelocenium chloride) rapidly decomposes to Ni^{2+} and a yellow deposit of the polymer,[76] i.e. nickelocene is extremely unstable in relation to ultraviolet irradiation.

V. PRACTICAL APPLICATIONS OF METALLOCENES IN PHOTOCHEMICAL PROCESSES

Patent data on the use of ferrocene as the main component of a light-sensitive composition were published in 1965.[77–79] Apart from ferrocene, CBr_4 and tone-controlling compounds were introduced into the light-sensitive composition. On exposure to light from an incandescent lamp and subsequent thermofixation, brown-violet images were obtained.

Highly sensitive materials have been developed on the basis of ferrocene, CBr_4 and a polymeric binder.[80] Subsequent studies designed to improve the compositions based on a number of ferrocene derivatives led to the creation of a whole series of light-sensitive materials. Light-sensitive emulsions containing ferrocene derivatives, a halogenohydrocarbon, and indole have been developed. The ferrocene derivatives employed were 1,1′-diacetylferrocene, 1,1′-dipropionylferrocene, 1,1′-dibenzoylferrocene, 4-(dimethylamino)-benzoylferrocene, and ferrocenedicarboxylic acid. A characteristic feature of these emulsions is their photosensitivity in the visible region of the spectrum.[81,82] It has been established that, by introducing aromatic aldehydes[83,84] into these photosensitive emulsions, it is possible to obtain multi-coloured images. In this connection it has been stated that in the presence of aldehydes[85] a deepening of the colour of the resulting image is achieved and the image becomes more distinct; the causes of this phenomenon are not discussed in the relevant patent.

Copying materials for microfilming,[86] containing polyvinylcarbazole, ferrocene, halogenohydrocarbons, and aromatic aldehydes have been described. Light-sensitive compositions based on imidazole derivatives, halogeno-derivatives, and ferrocene have been developed in the Federal Republic of Germany.[87]

Later, as the chemistry of ferrocene developed, more complex ferrocene-containing compounds began to be introduced into light-sensitive compositions.[88] A photographic material in which an emulsion containing ferrocene derivatives having the general formula

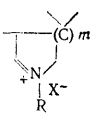
$$X{-}C_5H_4FeC_5H_4{-}Y$$

X=CO(CH=CH)$_n$ Ar; n = 1, 2; Y=H, X

was deposited on baryta paper has been described.[89,90] An alcoholic solution of the test substance was deposited onto baryta paper and the latter was dried. The exposure was under an incandescent 500 W lamp for 5–11 min. In order to remove the unexposed sections, the emulsions were treated with solvents, which consisted of methanol or ethanol. The images obtained were predominantly of a yellowish-red colour.

It is noteworthy that water-soluble materials have also been developed on the basis of ferrocene in which the light-sensitive components were ferrocene-containing dyes[91] of the type

$$C_5H_5FeC_5H_4{-}(CH{=}CH)_{n+1}R' \quad \text{or} \quad C_5H_5FeC_5H_4{-}(CH{=}CH)_n{-}$$



R = alkyl; R′ = pyrylium salt;

X=Cl′, Br, I; n = 1–3; m = 1, 2.

When vinyl groups are introduced, a long conjugated system is created and the absorption maximum of these compounds undergoes a bathocromic shift. The dyes synthesised were used to obtain light-sensitive materials which suffered from the disadvantage of a comparatively low light-sensitivity: in order to obtain a visible image, the emulsions had to be exposed for 4–6 min under a 2000 W lamp and then heated to 150 °C.

Charge-transfer complexes based on ferrocene, vinylferrocene, and various electron acceptors, which possess light-sensitive properties, have been recommended as optical filters absorbing in the range 350–600 nm.[92]

A negative light-sensitive material, sensitive both in the ultra-violet and in the visible part of the spectrum, has been prepared from ferrocene, halogeno-derivatives, and tone-controlling compounds with addition of polystyrene dissolved in trichloroethane.[93]

A light-sensitive composition for lithographic plates[94] has been obtained from a polymer with unsaturated ethylene groups or groups containing two or three chlorine or bromine atoms linked to one carbon atom and ferrocene derivatives (for example, thioacetylferrocene and 1,1'-dicinnamoylferrocene).

There have been a number of studies devoted to the mechanism of the intensification of the latent image in light-sensitive emulsions based on ferrocene.[95-97]

In 1971 a copying material containing the ammonium salt of ferrocenemonosulphonic acid or ferrocenedisulphonic acid or their mixture as well as a phenol residue containing the amino-, hydroxy-, or carbonyl groups in the *ortho*-position was developed in Japan in 1971.[98] A composition based on an organohalogen compound and a copolymer containing vinylferrocene and hardening on exposure to light has been patented.[99] Similar copolymers based on vinylferrocene are used in various photographic materials.[100] A patent[101] describes a positive material, sensitive to electrons and X-rays and other types of radiation, containing a copolymer of 1–30 mole % of vinylferrocene and 70–99 mole % of methacrylic acid.

A composition containing an organic halogen compound, aniline dyes, and ferrocene has been recommended for the formation of a coloured image.[102] A light-sensitive material for the formation of a black and white image by the dry method and based on ferrocene, organic dyes, and a halogeno-derivative giving rise to free radicals under the influence of light has been described.[103]

It is noteworthy that the entire patent literature contains as a rule only qualitative descriptions of light-sensitive compositions and emulsions based on them. In the literature there are virtually no physicochemical data and sensitometric and other characteristics of the materials obtained; it is therefore impossible to carry out an objective assessment of the light-sensitive characteristics of the proposed compositions or reach any conclusions about the likely usefulness of a particular composition from the standpoint of its practical applications.

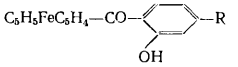
Metallocene derivatives are also used as photoconductors in electrophotography. Ferrocene, cobaltocene, and nickelocene have found the most extensive applications for these purposes.[104,105] Styrenebutadiene raw rubbers are used as binders and pyrylium salts are added as sensitisers.

The product of the condensation of formylferrocene with added organic halogeno-derivatives has been proposed for the preparation of polymeric ferrocene-containing emulsions for electrophotography.[106,107] A high-quality electrophotographic material has been obtained on the basis of polyvinylferrocene.[108] It permitted the repeated recording of an image.

When aromatic amino-derivatives, dyes, halogenohydrocarbons, and organometallic compounds[109] (ferrocene and cobaltocene) are added to a photoconductor based on polyvinylcarbazole or its brominated analogue, the photoconduction process is accelerated.[110] Thus a photoconductor containing cobaltocene can be exposed at 80 lux, while in the absence of added cobaltocene the exposure is 280 lux. It has been suggested that nickelocene be also used for these purposes.[111] A photoconducting composition suitable for the preparation of copying photoconductive emulsions based on polymeric compounds derived from formylferrocene has been obtained.[112]

It has been reported that metallocenes behave as photoinitiators in polymerisation.[113,114]

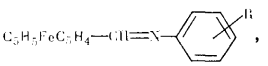
It is known that many ferrocene derivatives are capable of photostabilising various polymers.[115,116] For example, derivatives of hydroxybenzoylferrocene are used to stabilise polyolefins:[117]



R=OH, NO_2, C_2H_5, C_6H_5, $COCH_3$, COOH

Oxygen-containing,[118-120] silicon-containing,[121] and other derivatives of ferrocene[122] have been proposed as light stabilisers for polymers.

In order to improve the resistance of polyethylene to ultraviolet radiation, the oxime of acetylferrocene[123] or ferrocene-containing azomethines,[124] having the general formula



R = H, OH,

are introduced into the polymer.

The influence of ferrocene added to high-pressure polyethylene on the photodegradation of the polyethylene film has been investigated. It has been suggested that ferrocene and its derivatives catalyse the radical decomposition of the hydroperoxy-groups in polyethylene. The addition of ferrocene and its derivatives can be used to obtain materials which rapidly decompose under natural conditions.[125]

As can be seen from the foregoing, the photochemical processes involving metallocenes proceed as a rule via two pathways: either with the consumption of the metallocenes or with retention of the metallocene system and the formation of the product of substitution in the cyclopentadienyl ring. The photolysis of ferrocenium salts results in the formation of mainly ferrocene.

The photochemistry of ruthenocene has much in common with that of ferrocene. Analysis of the literature data on the photochemistry of metallocenes permits the conclusion that metallocenes containing an even total number of valence electrons are more stable, whereas those with an odd number of valence electrons are less stable.

Studies of the photochemical transformations in metallocenes are of great interest, since they make it possible to develop on the basis of these compounds materials which are finding practical applications in various systems for the recording, treatment, and replication of information.

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Moscow Textile Institute

Translated from *Uspekhi Khimii*, 54, 2024-2055 (1984) U.D.C. 546.162

Halogen Fluorides in Organic Synthesis

L.S. Boguslavskaya

The reactions of halogen fluorides with organic compounds are considered and the possibilities for their employment as selective fluorinating agents for the synthesis of organic mono- and poly-fluoro-compounds are discussed. The reactivities of halogen monofluorides are compared with those of their stoichiometric equivalents. The mechanisms of the reactions of halogen fluorides and their inorganic complexes are discussed.
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I. INTRODUCTION

The unusual practical value of organofluorine compounds for modern technology, medicine, and agriculture has stimulated chemists to seek continuously new and selective methods for the introduction of fluorine into an organic molecule. The endeavour to "tame" molecular fluorine, to bind it in a milder fluorinating agent, has for many years occupied the minds of chemists specialising in organofluorine chemistry. From this standpoint, halogen fluorides have attracted the attention of investigators for a long time.[1] Until recently, despite the well-developed technical methods for their synthesis and the commercial availability of some of them, these reagents have been hardly used in organic synthesis.[1-5] The idea arose that halogen fluorides are almost as corrosive as molecular fluorine[4] and therefore their applications are restricted to reactions with polyfluorinated compounds. It was difficult to expect that, being so corrosive, halogen fluorides would find applications in the controlled fluorination of polyhydro-compounds. In reactions with unsaturated polyhydro-compounds, only the stoichiometric equivalents of halogen monofluorides, namely "HalF *in situ*", obtained mainly from *N*-halogenoamides in anhydrous hydrogen fluoride, have been investigated.[4-6]

Nevertheless in recent years, preparative possibilities of halogen fluorides have been discovered and experimental data have accumulated which make it possible to regard certain halogen fluorides, particularly chlorine monofluoride, as promising selective fluorinating agents.

Chlorine monofluoride is of special interest also from the standpoint that it can be obtained and used in synthesis in two ways: gaseous ClF can be obtained from the elements and introduced into the reaction with the substrate in both non-polar and polar media; the "stoichiometric equivalents of ClF", obtained from *N*-chloroamides (or *N*-chloroamines) in HF, always react in a polar medium. Comparison of the results of these reactions permits well-founded conclusions about the mechanism of fluorination by halogen fluorides.

This review deals with the synthetic aspects of reactions involving fluorination by halogen fluorides and provides a critical survey of studies on the mechanism of these and related reactions.

II. THE SYNTHESIS AND PROPERTIES OF HALOGEN FLUORIDES

Halogen fluorides have been obtained and widely used by inorganic chemists because at one time they found applications in the atomic industry for the synthesis of uranium and other metal fluorides and also as powerful oxidants in rocket engineering.[2,3,5] Virtually all halogen fluorides have been synthesised directly from the elements. Gaseous chlorine monofluoride is obtained by passing stoichiometric amounts of chlorine and fluorine through heated copper or nickel tubes:[7-10]

$$Cl_2 + F_2 \xrightarrow{200-250^\circ} 2ClF\ .$$

The design and materials of the apparatus, the conditions of the synthesis, and the kinetics of the process have been described in detail in a monograph[2] and in recent communications.[8,10] In the laboratory, chlorine monofluoride can also be obtained by mixing theoretical amounts of chlorine trifluoride and chlorine at 350 °C [11] or by passing chlorine into a melt of alkali metal fluorides at 800–1000 °C:[12]

$$Cl_2 + MF \rightleftarrows MCl + ClF\ ;$$
$$M=K,\ Na,\ Li\ .$$

A method of synthesis of ClF by passing chlorine into a solution of SbF_5 in anhydrous HF at 35 °C has been patented.[13] Chlorine trifluoride is a low-boiling liquid and is an industrial product. The methods of its synthesis and apparatus have been described in detail.[1,2] ClF_3 is usually synthesised from chlorine monofluoride and fluorine or directly from chlorine and fluorine:

$$ClF + F_2 \xrightarrow{250-280^\circ} ClF_3\ .$$

Chlorine trifluoride is condensed, purified by fractionation, and stored in cylinders.

Chlorine pentafluoride (a low boiling liquid; at abient temperature—a gas) is difficult to obtain. It can be synthesised from chlorine trifluoride and fluorine by heating under

high pressure[14] or in quartz apparatus under ultraviolet irradiation:[15]

$$ClF_3 + F_2 \xrightarrow[250\ atm]{350^\circ} ClF_5 ;$$

$$ClF_3 + F_2 \xrightarrow[30^\circ]{h\nu} ClF_5 .$$

Bromine monofluoride is a low-boiling unstable liquid, which has been obtained from the elements at +10 °C and purified by successive condensation of the impurities.[16,17] BrF is usually contaminated with bromine and bromine polyfluorides owing to its tendency to disproportionate:[18,19]

$$Br_2 + F_2 \xrightarrow{10^\circ} 2BrF ;$$

$$3BrF \rightarrow Br_2 + BrF_3 .$$

Bromine trifluoride is a stable liquid and is manufactured industrially by passing purified fluorine into liquid bromine in copper apparatus with subsequent vacuum distillation of the product. The design of the apparatus and the technique of the synthesis have been described in detail:[1,2]

$$Br_2 + 3F_2 \xrightarrow{80^\circ} 2BrF_3 .$$

Bromine pentafluoride is an entirely stable product; it is produced industrially directly from bromine and fluorine:[1,2]

$$Br_2 + 5F_2 \xrightarrow{200^\circ} 2BrF_5 .$$

Among iodine fluorides, only IF_5 and IF_7 are stable. The methods of their synthesis from the elements have been described in detail.[1-3] Iodine pentafluoride can be obtained also from chlorine trifluoride and iodine, their interaction occurring with spontaneous combustion in accordance with the equation[2]

$$10\,ClF_3 + 3I_2 \rightarrow 6IF_5 + 5Cl_2 .$$

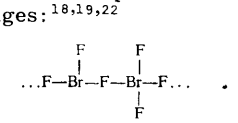
Iodine pentafluoride is a colourless liquid which can be stored in quartz or steel vessels.

Iodine heptafluoride is a colourless gas and has been obtained from the elements in platinum apparatus at high temperatures.[2] Iodine pentafluoride is formed initially and then absorbs fluorine under more severe conditions and is converted into IF_7:

$$I_2 + 5F_2 \rightarrow 2IF_5 ;$$

$$IF_5 + F_2 \xrightarrow{250-280^\circ} IF_7 .$$

Table 1 presents the physical properties of halogen fluorides and, for comparison, those of the molecular halogens. Halogen fluorides are polar compounds and have significant dipole moments. Chlorine and bromine monofluorides have comparatively high dissociation energies $E_d \cong 60$ kcal mol^{-1}. Hence the tendency of these interhalogen compounds to undergo heterolysis rather than homolysis is understandable. The dissociation energies of halogen polyfluorides (ClF_3, IF_7) are actually lower than that of molecular fluorine and hence one may expect their ready decomposition into free radicals. It is striking that the boiling points of halogen fluoride are significantly higher than might have been expected from their molecular weights. Their low volatility can be accounted for by the ability of these compounds to associate with formation of fluorine bridges:[18,19,22]



An important property of halogen fluoride is their amphoteric behaviour. Thus bromine trifluoride is capable of self-ionisation:[23]

$$BrF_3 \rightleftarrows BrF_2^+BrF_4^- .$$

Halogen fluorides react with Lewis acids and bases forming complex fluorine-containing cations and anions:[2,23,24]

$$XF_n + YF_m \rightarrow XF_{n-1}^+YF_{m+1}^- ;$$

$$XF_n + MF \rightarrow M^+XF_{n+1}^- .$$

Compounds of this type are interesting because they can be used as fluorinating agents, which are frequently more convenient to handle than the halogen fluorides themselves.

Table 1. The physical properties of the halogens and halogen fluorides.[2,5,20,21]

Compound	B.p., °C	M.p., °C	Dipole moment, D	Interatomic distances, Å	E_d, kcal mol^{-1}
F_2	−188	−219	—	1.418	38
Cl_2	−35	−101	—	1.988	58
ClF	−100	−155	0.89	1.63	61
ClF_3*	+12	−76	0.65	1.598; 1.698	25
ClF_5**	−13	−93	—	—	—
Br_2	+59	−7	—	2.284	46
BrF	+20	−33	1.29	—	60
BrF_3*	+126	+9	1.19	1.72; 1.81	—
BrF_5**	+41	−30	1.51	1.68; 1.78	—
I_2	+184	+113	—	2.666	36
IF	+1 (decomp.)	—	—	—	58
IF_3*	−35 (decomp.)	—	—	—	—
IF_5**	+100	+9	2.18	—	66
IF_7	+5 (sublimes)	+6	—	—	29

*Planar T-shaped structure.
**Tetragonal pyramid.

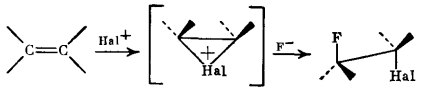
III. THE REACTIONS OF BROMINE AND IODINE MONOFLUORIDES

Bromine and iodine monofluorides are unstable compounds and have therefore been little studied as such in organic synthesis, although the reactions of their stoichiometric equivalents "BrF" and "IF" have been studied quite widely.

1. The Reactions of the Stoichiometric Equivalents "BrF" and "IF"

The *N*-bromoamide or *N*-iodoamide–anhydrous hydrogen fluoride systems[4,6] and more rarely the molecular halogens Br_2 or I_2 in anhydrous hydrogen fluoride[25-27] as well as Br_2–AgF [28,29] constitute the stoichiometric equivalents of BrF and IF. As will be shown below, this does not by any means imply that bromine and iodine monofluorides are actually formed in such systems. *N*-Halogenoamides of molecular halogens are sources of the electrophilic halogen, while HF or AgF provide the nucleophile—the fluoride anion.

In essence, the only application of these systems involves the addition of BrF and IF to a multiple bond. As a rule, halogenofluorination proceeds under mild conditions—at temperatures ranging from −80 °C to room temperature.[4,30] Electron-donating substituents at the multiple bond accelerate while electron-accepting substituents retard their reaction.[31] The halogenofluorination by such systems is a typical electrophilic addition reaction:



A multiplicity of preparative modifications of halogenofluorination depending on the type of unsaturated compound and the source of the electrophilic halogen are known. Oxygen-containing solvents, namely ether and tetrahydrofuran,[4,30] 70 : 30 HF-pyridine,[25,26,32] or anhydrous HF without a solvent[31] are used. The application of oxygen-containing solvents is not always desirable, since they can participate in the addition reaction as nucleophiles.[33,34] Halogenofluorination in a hydrogen fluoride–pyridine mixture gives fairly satisfactory yields in the case of phenylolefins.[25,26,32,35,36] Electrophilic halogenation of the aromatic ring does not then occur. The influence of substituents at the multiple bond on the regiospecificity and stereochemistry of the bromofluorination has been thoroughly investigated (Table 2).

Table 2. The regiospecificity and stereochemistry of the bromofluorination of substituted olefins by *N*-bromoamides in anhydrous hydrogen fluoride.

No.	Initial olefin	Regiospecificity, %		Stereospecificity,* %	Refs.
		$>C^1(Br)-C^2(F)<$	$>C^1(F)-C^2(Br)<$		
1	$C^1H_2=C^2Cl_2$	100	0	—	[37]
2	*Z*-$CHCl=CHCl$	—	—	100	[37]
3	*E*-$CHCl=CHCl$	—	—	85	[37]
4	$CH_2=C^2HCH_2Cl$	40	60	—	[38]
5	*Z*-$C^1HCl=C^2HCH_2Cl$	0	100	100**	[39]
6	*E*-$C^1HCl=C^2HCH_2Cl$	0	100	100	[39]
7	*Z*-$C^1HCl=C^2(Me)CH_2Cl$	100	0	100	[27]
8	*E*-$C^1HCl=C^2(Me)CH_2Cl$	100	0	100	[27]
9	*Z*-$C^1HCl=C^2ClCH_2Cl$	100	0	100	[27]
10	*E*-$C^1HCl=C^2ClCH_2Cl$	100	0	60	[27]
11	*Z*-$C^1HCl=C^2FCH_2Cl$	100	0	—	[27]
12	*E*-$C^1HCl=C^2FCH_2Cl$	100	0	—	[27]
13	$C^1H_2=C^2HCOOMe$	—	>90	—	[33]
14	$C^1H_2=C^2(Me)COOMe$	100		—	[40]
15	*E*-$C^1HCl=C^2(Me)COMe$	0	100	100	[31,41]
16	*Z*-$C^1HCl=C^2ClCOOMe$	30	70	100	[31,41]
17	*Z*-$C^1HCl=C^2FCOOMe$	22	78	100	31,41]
18	*Z*-$CH_3C^1Cl=C^2HCOOEt$	0	100	65	[41]
19	*E*-$CH_3C^1Cl=C^2HCOOEt$	0	100	70	[41]
20	*Z*-$CH(COOMe)=CHCOOMe$	—	—	100	[33]
21	*E*-$CH(COOMe)=CHCOOMe$	—	—	100	[33]
22	$C^1H_2=C^2HPh$	100	0	—	[35]
23	$C^1H_2=C^2Ph_2$	100	0	—	[35]
24	$C^1HF=C^2Ph_2$	100	0	—	[35]
25	$C^1HCl=C^2Ph_2$	100	0	—	[35]
26	$C^1HBr=C^2Ph_2$	100	0	—	[35]
27	$C^1H_2=C^2(Me)Ph$	100	0	—	[35]
28	$C^1H(CH_3)=C^2Ph_2$	100	0	—	[35]
29	*Z*-$C^1HBr=C^2HPh$	100	0	—	[35]
30	*E*-$C^1HBr=C^2HPh$	100	0	—	[35]
31	*Z*-$C^1H(Me)=C^2HPh$	100	0	65**	[35]
32	*E*-$C^1H(Me)=C^2HPh$	100	0	100	[35]
33	*Z*-$CHPh=CHPh$	—	—	70**	[35]
34	*E*-$CHPh=CHPh$	—	—	100	[35]
35	*Z*-$(Me)_3CC^1H=C^2HPh$	100	0	0**	[35]
36	*E*-$(Me)_3CC^1H=C^2HPh$	100	0	100	[35]
37	*Z*-$C^1H(COOEt)=C^2HPh$	100	—	100	[32]
38	*E*-$C^1H(COOEt)=C^2HPh$	100	—	100	[32]
39	*Z*-$C^1F(COOEt)=C^2HPh$	100	—	100	[32]
40	*E*-$C^1F(COOEt)=C^2HPh$	100	—	100	[32]
41	*Z*-$C^1Cl(COOEt)=C^2HPh$	100	—	100	[32]
42	*E*-$C^1Cl(COOEt)=C^2HPh$	100	—	100	[32]
43	*Z*-$C^1H(COOEt)=C^2ClPh$	100	—	50	[32]
44	*E*-$C^1H(COOEt)=C^2ClPh$	100	—	50	[32]

*The content of the *anti*-adduct.
**The *Z*-isomer is partly converted into the *E*-isomer during synthesis.

On the whole, the mode of addition of the electrophile and nucleophile expected for an electrophilic mechanism is observed. Since unsaturated compounds with electron-deficient multiple bonds, which usually react with the halogens via a free-radical mechanism, can be introduced into the bromofluorination reaction, it is of interest to compare the competing influences of the substituents on the mode of addition and the stereochemical characteristics of the bromofluorination.

The bromofluorination of 1,3-dichloroprop-1-enes (Table 2, Nos. 5 and 6) proceeds regiospecifically in such a way that the electrophilic bromine is directed to the central carbon atom, while the nucleophile F^- ion is directed to the terminal carbon atom:

$$CHCl=CHCH_2Cl \xrightarrow[HF]{>NBr} CHClFCHBrCH_2Cl .$$

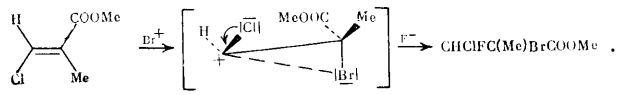
The chlorine atom attached to the multiple bond behaves as a *p*-donor and fully controls the mode of addition. The introduction into the 2-position of 1,3-dichloropropene of substituents delocalising the positive charge of the carbonium ion completely alters the mode of addition—the electrophile is directed to the terminal carbon atom, while the nucleophile goes to the central carbon atom (Table 2, Nos. 7–12):

$$CHCl=CRCH_2Cl \xrightarrow[HF]{>NBr} CHClBrCRFCH_2Cl ;$$

$$R=CH_3,\ Cl,\ F .$$

Overall, the CH_2Cl and CH_3, F, or Cl substituents exhibit a more powerful directing effect than the chlorine atom.

An analogous effect has been observed in the bromofluorination of acrylates. Methyl acrylate is brominated almost entirely contrary to the Markovnikov rule (Table 2, No. 13), while methyl methacrylate is brominated in accordance with the Markovnikov rule (Table 2, No. 14). *p*-Donor substituents have a significantly greater stabilising influence on the intermediate carbonium ion than the CH_3 group. This is readily seen in relation to the bromofluorination of the methyl esters of α-R-β-chloroacrylic acids (Table 2, Nos. 15–17):

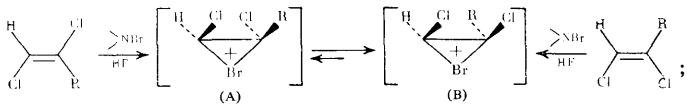


In the methyl ester of *E*-α-chloro-β-methylacrylic acid (Table 2, No. 15) the chlorine substituent fully controls the mode of addition—the reaction is regiospecific. The bromofluorination of the double bond in the methyl esters of αβ-dihalogenoacrylic acids is non-regiospecific (Table 2, Nos. 16 and 17). The phenyl group as the π-donor is a significantly more effective directing group than the halogen as the *p*-donor (Table 2, Nos. 29 and 30): the phenyl group controls the addition of BrF to 1-bromo-2-phenylethylenes:

$$CHBr=CHPh \xrightarrow[HF]{>NBr} CHBr_2CHFPh .$$

The bromofluorination of multiple bonds takes place mainly stereospecifically as an *anti*-addition reaction. In a number of instances (Table 2, Nos. 2, 3, 32, 34, and 36) this has been demonstrated reliably by the stereospecific dehydrobromination of the diastereoisomers obtained to the corresponding fluoro-olefins. The observed discrepancies, namely incomplete *anti*-stereospecificity (Table 2, Nos. 3, 10, 18, 19, 31, and 33) or *syn*-addition (Table 2, No. 36), can be convincingly accounted for by taking into account the known conditions governing the stability of bridged bromonium and open-chain carbenium ions, which are evidently intermediates in bromofluorination in hydrogen fluoride. The complete *anti*-stereospecificity of the addition of BrF to *E*-1,2-dichloroethylene and *E*-1,2,3-trichloropropene (Table 2, Nos. 3 and 10) can be explained by the fact that the bromonium ions (A) with transoid chlorine atoms are less stable than

the ions (B) with cisoid chlorine atoms, just as *trans*-dihalogenoethylenes are less stable than *cis*-dihalogenoethylenes:[42,43]

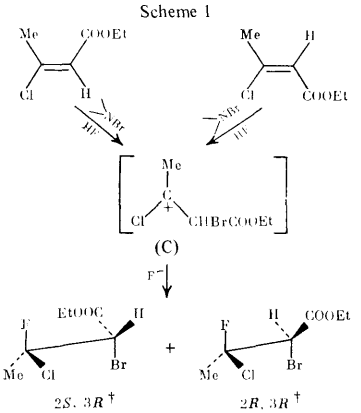


(A) (B)

R = H, CH_2Cl.

Because of this factor, the partial rearrangement of the ion (A) to the ion (B) takes place. For this reason, the bromofluorination of *Z*-olefins is fully *anti*-stereospecific (Table 2, Nos.2 and 9), while the bromofluorination of *E*-olefins (Table 2, Nos.3 and 10) is only stereoselective (85 and 60% of the *anti*-adducts respectively). The non-stereospecific addition of BrF to the ethyl esters of *E*- and *Z*-β-chlorocrotonic acids (Table 2, Nos.17 and 18) can be accounted for by other causes[41] (Scheme 1). The addition of electrophilic bromine to the double bond in β-chlorocrotonates results in the formation of an intermediate which is in essence not a bromonium ion but an open-chain carbenium ion (C). This is promoted by the two geminal substituents (the methyl group and the chlorine atom) at the carbonium ion centre, which stabilise carbonium ions, and by the electron-accepting alkoxycarbonyl group at the vicinal carbon atom. As a result, the reaction is regiospecific and non-stereospecific.

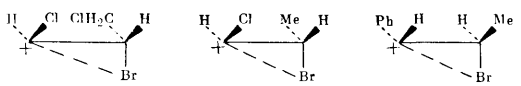
Scheme 1



(C)

2*S*, 3*R*† 2*R*, 3*R*†

However, the examples in Table 2 (compounds Nos.5, 6, 14, 32, and 37–42) show that even a weak *p*-bridge bond in the asymmetric bromonium ions (D), (E), and (F) is sufficient for the fully regiospecific reaction to proceed as an *anti*-stereospecific process.



(D) (E) (F)

The deviations of the bromofluorination of phenylethylenes from *anti*-stereospecificity (Table 2, Nos.31, 33, and 35) are associated with the fact that during the reaction *cis*-olefins isomerise to the more stable *trans*-olefins.[35] In the case of the sterically very greatly hindered *cis*-1-t-butyl-2-phenylethylene, *syn*-addition is observed exclusively.

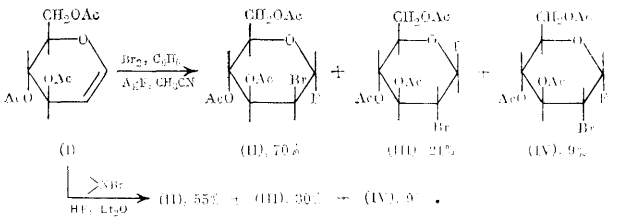
† One enantiomer is shown in Scheme 1 for each diastereoisomer. Owing to the incorrect designation of the sequence of substituents in terms of priority, in the original communications[31,41] incorrect names in terms of the *R*,*S*-system are given under the corresponding perspective formulae.

It has been reported[44–47] that cyclic unsaturated sugars, namely acetylated glucals, are iodofluorinated and bromofluorinated by *N*-iodo- and *N*-bromo-succinimide in hydrogen fluoride with formation of *syn*-adducts. In a later study[28] it was shown with the aid of ^1H and ^{19}F NMR that these reactions proceed predominantly as *anti*-addition and that the assignment of the configurations of the halogenated sugars in earlier studies[44–47] was incorrect.

A system containing a molecular halogen (Br_2, I_2), finely ground silver fluoride, and benzene or its mixture with acetonitrile as the solvent has been recommended[28,29,48] for the successful halogenofluorination of unsaturated sugars and other compounds which readily polymerise or rearrange in hydrogen fluoride.

On treatment with both Br_2–AgF and *N*-bromosuccinimide in hydrogen fluoride, *anti*-adducts are formed from the glucal triacetate (I) (Scheme 2)—2-bromo-2-deoxy-α-D-mannosyl fluoride triacetate (II) and 2-bromo-2-deoxy-α-D-glucopyranosyl fluoride triacetate (III), together with a small amount of the *syn*-adduct, namely the β-anomer (IV).[28,29]

Scheme 2

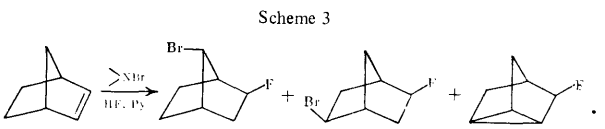


(I) (II), 70% (III), 21% (IV), 9%

(II), 55% + (III), 30% + (IV), 9%

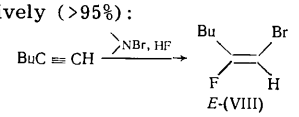
The bromofluorination of norbornene and related compounds by *N*-bromosuccinimide and hydrogen fluoride in ether or pyridine is accompanied by the Wagner–Meerwein rearrangement.[25,49–51] Norbornene gives rise to three main products (Scheme 3): 7-*anti*-bromo-2-*exo*-fluoronorbornane (V), 5-*exo*-bromo-2-*exo*-fluoronorbornane (VI), and 3-fluoronortricyclene (VII).

Scheme 3

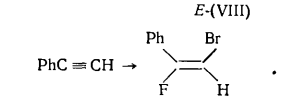


(V), 37% (VI), 35% (VII), 20%

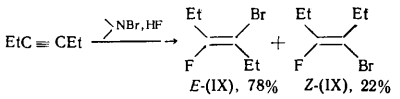
The regiospecificity and stereochemistry of the bromofluorination of substituted acetylenes by *N*-bromoacetamide in anhydrous hydrogen fluoride has been investigated.[52] Vicinally substituted bromofluoroalkenes can be obtained with the aid of this reaction in satisfactory yields, but treatment of substituted acetylenes with the Br_2–AgF system resulted in the formation of bromination products only. The bromofluorination of terminal acetylenes takes place regiospecifically in conformity with the Markovnikov rule and *anti*-stereoselectively (>95%):



E-(VIII)



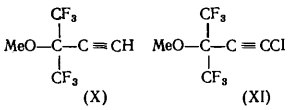
The product of the bromofluorination of hex-1-yne, namely *E*-1-bromo-2-fluorohex-1-ene (VIII), gradually isomerises on storage to the thermodynamically more favourable *Z*-isomer; a 60 : 40 mixture of the *E*- and *Z*-isomers of compound (VIII) is formed after one month, which indicates the kinetic control of the bromofluorination of hex-1-yne. Hex-3-yne is bromofluorinated non-stereospecifically with formation of 78% of the *anti*-adduct and 22% of the *syn*-adduct (IX):



E-(IX), 78% *Z*-(IX), 22%

The mixture of the bromofluoroadducts (IX) does not undergo a change in composition on storage for 15 months.

1,4-Dichlorobut-2-yne gives rise to only one bromofluoroadduct, probably as a result of the *anti*-addition, but the configuration of the resulting 2-bromo-1,4-dichloro-3-fluorobut-2-ene has not been demonstrated.[52] The influence of the structure of acetylenes on the ease of their bromofluorination has been noted: the halogenoacetylenes (X) and (XI) are not bromofluorinated at all under these conditions:



(X) (XI)

The observed facts show that the intermediates in the bromofluorination of acetylenes have the character of oriented π-complexes which differ from the classical carbonium ions; otherwise a lower stereospecificity would have been expected.

It has been reported that the iodofluorination of 1-phenylalk-1-ynes by methyl iodide difluoride (CH_3IF_2) takes place as *syn*-addition.[53]

2. Fluorination by Bromine and Iodine Monofluorides

Mixtures of stoichiometric amounts of bromine trifluoride and molecular bromine or of iodine pentafluoride and molecular iodine have been used as sources of bromine and iodine fluorides in reactions involving addition to perfluoro- and chlorofluoro-olefins[54–58] and also to alkyl perfluoroalkenyl ethers:[57]

$$BrF_3 + Br_2 \rightleftarrows 3BrF \ ;$$
$$IF_5 + 2I_2 \rightleftarrows 5IF \ .$$

Evidence has been obtained that BrF is indeed formed in a mixture of bromine trifluoride and bromine.[59] The reactions of these systems with olefins have been achieved in steel apparatus in the temperature range from 20° to 150–170 °C. The corresponding adducts have been obtained in most cases in exceptionally high yields. The mode of addition of IF and BrF to certain olefins indicates an electrophilic mechanism of the reaction:[54–57]

$$CF_2{=}CH_2 \xrightarrow[100°]{IF_5-I_2} \underset{86\%}{CF_3CH_2} \ ;$$
$$CF_2{=}CFCF_3 \xrightarrow[20°]{BrF_3-Br_2} \underset{46\%}{(CF_3)_2CFBr} \ ;$$
$$(CF_3)_2CFCF{=}CFCF_3 \xrightarrow[40-50°]{BrF_3-Br_2} \underset{29\%}{(CF_3)_2CFCF_2CFBrCF_3} + \underset{29\%}{(CF_3)_2CFCFBrCF_2CF_3} \ ;$$
$$(CF_3)_2C{=}CFOMe \xrightarrow[0°]{BrF_3-Br_2} \underset{43\%}{(CF_3)_2CBrCF_2OMe} \ .$$

The interaction of ethyl perfluoroalkenyl ethers with the BrF_3–Br_2 system involves the substitution of the α-hydrogen atom in the ethyl group by fluorine together with the addition of BrF to the double bond:[57]

$$(CF_3)_2C{=}CFOEt \xrightarrow[60°]{BrF_3-Br_2} \underset{28\%}{(CF_3)_2CBrCF_2OCHFMe} \ .$$

The BrF_3–Br_2 system has been used for the substitutional fluorination of bromopolyfluoroalkanes.[60] The gradual addition of a solution of the bromofluoroalkane in molecular bromine to a mixture of BrF_3 with bromine at 0–50 °C leads to substitution products in a high yield:

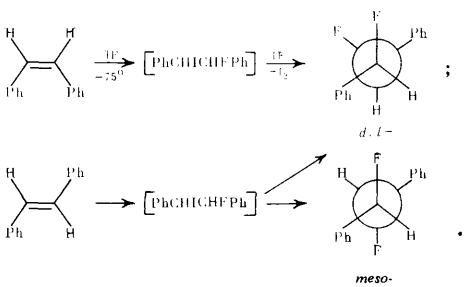
$$CF_3CHBr_2 \xrightarrow[25-35°]{BrF_3-Br_2} \underset{92\%}{CF_3CHBrF} + \underset{5\%}{CF_3CHF_2} \ ;$$
$$CF_2BrCHBr_2 \rightarrow \underset{77\%}{CF_3CHBrF} \ ;$$
$$CF_2BrCBr_3 \rightarrow \underset{79\%}{CF_2BrCFBr_2} + \underset{4\%}{CF_2BrCF_2Br} \ .$$

A possible mechanism has been proposed for the substitutional fluorination taking into account the tendency of bromine to undergo self-ionisation:

$$2BrF_3 \rightarrow BrF_2^+BrF_4^- \ ;$$
$$-\overset{|}{\underset{|}{C}}Br + BrF_2^+ \rightarrow \left[-\overset{|}{\underset{|}{C}}{}^{\delta+} \cdots Br^{\delta-} \cdots Br^{\delta+}\begin{matrix}F\\F\end{matrix}\right] \rightarrow -\overset{|}{\underset{|}{C}}{}^{+} + Br_2F_2 \ ;$$
$$-\overset{|}{\underset{|}{C}}{}^{+} + BrF_4^- \rightarrow -\overset{|}{\underset{|}{C}}F + BrF_3 \ .$$

Since chlorine monofluoride readily enters into an analogous fluorination reaction in a non-polar medium (see below), it is extremely likely that a molecule of bromine monofluoride participates in the electrophilic debromofluorination.

In a recently published study[61] iodine monofluoride was obtained by passing molecular fluorine diluted with nitrogen into a solution of iodine in trichlorofluoromethane (Freon) at −75 °C. By adding olefins to the resulting cold IF solution in Freon, fluoroiodoalkanes were synthesised in satisfactory yields. 2-Fluoro-1-iodo-octane (70%), *trans*-1-fluoro-2-iodocyclohexane (64%), etc. have been obtained by this method. The iodofluorination of *cis*- and *trans*-stilbenes by this procedure is accompanied by further substitution of the iodine in the fluoroiodoadducts by fluorine. The unusual stereochemistry of these reactions has been noted: only *dl*-1,2-difluoro-1,2-diphenylethane has been obtained from *cis*-stilbene, while *trans*-stilbene gave rise to a mixture of the *meso*- and *dl*-diastereoisomers in proportions of 1 : 1:



d,l-

meso-

IV. THE REACTIONS OF CHLORINE MONOFLUORIDE

Chlorine monofluoride is the only gaseous reagent among all the halogen fluorides which is stable under the usual conditions and is therefore the most convenient. ClF can be readily obtained from the molecular halogens (see Section II) and can be immediately brought into contact with the organic substrate in rigorously controlled amounts, which makes it possible to regulate the process. In recent years this reagent has attracted the continuous attention of chemists concerned with organofluorine chemistry, as shown by a recently published review.[62] The data obtained after the publication of this review illustrate the new possibilities for chlorine monofluoride in the fluorination of organic compounds and make it possible to consider certain general theoretical aspects of the reactions of electrophiles.

1. The Reactions of the Stoichiometric Equivalents "ClF"

The *N*-chloroamide–HF,[25] the hexachloromelamine–HF,[63] or the molecular chlorine–HF [63,64] systems serve as sources of "ClF". It has been reported that, in the presence of boron trifluoride, methyl hypochlorite is also capable of chlorofluorinating unsaturated compounds.[65] The conditions under which the reactions involving the chlorofluorination of unsaturated compounds take place differ little from the bromofluorination conditions; depending on the type of substrate, the reactant ratio, and the solvent, the yields attained (with respect to the initial alkene) are 30–80%.[25–27, 31,37,41,66–75] The regiospecificity and stereochemistry of the chlorofluorination of substituted olefins by the hexachloromelamine–HF system have been studied in greatest detail (Table 3).

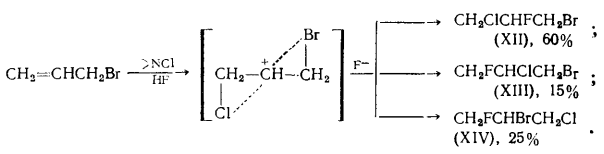
Table 3. The regiospecificity and stereochemistry of the chlorofluorination of substituted olefins by hexachloromelamine in anhydrous hydrogen fluoride.

No.	Initial olefin	Regiospecificity, %		Stereospecificity, %	Refs.
		>C¹(Cl)–C²(F)<	>C¹(F)–C²(Cl)<		
1	$C^1H_2{=}C^2Cl_2$	100	0	—	[37]
2	$C^1H_2{=}C^2HCH_2OH$	90	10	—	[66]
3	$C^1H_2{=}C^2HCH_2OCOCF_3$	67	33	—	[67]
4	$C^1H_2{=}C^2HCH_2Cl$	68	32	—	[68]
5	$C^1H_2{=}C^2HCH_2Br$	60	40	—	[68]
6	$C^1H_2{=}C^2ClCH_2OH$	100	0	—	[69]
7	$C^1H_2{=}C^2FCH_2OH$	100	0	—	[69]
8	$C^1H_2{=}C^2ClCH_2Cl$	100	0	—	[70]
9	$C^1H_2{=}C^2FCH_2Cl$	100	0	—	[70]
10	Z-$C^1HCl{=}C^2HCH_2Cl$	0	100	93	[39, 71]
11	E-$C^1HCl{=}C^2HCH_2Cl$	0	100	87.5**	[39, 71]
12	$C^1HCl{=}C^2(Me)CH_2Cl$	100	0	—	[27]
13	$C^1HCl{=}C^2ClCH_2Cl$	100	0	—	[27]
14	$C^1HCl{=}C^2FCH_2Cl$	100	0	—	[27]
15	$C^1H_2{=}C^2HCOOMe$	19	81	—	[63, 72]
16	$C^1H_2{=}C^2(Me)COOMe$	95	5	—	[72, 73]
17	$C^1H_2{=}C^2(OMe)COOMe$	100	0	—	[74]
18	$C^1H_2{=}C^2(OAc)COOMe$	100	0	—	[74]
19	E-$C^1HCl{=}C^2(Me)COOMe$	0	100	100	[31, 41]
20	Z-$C^1HCl{=}C^2ClCOOMe$	35	65	—	[31]
21	Z-$C^1HCl{=}C^2FCOOMe$	8	92	100	[31, 41]
22	Z-$C^1Cl(Me){=}C^2HCOOEt$	0	100	50	[41]
23	E-$C^1Cl(Me){=}C^2HCOOEt$	0	100	50	[41]

*The content of the *anti*-adduct.
**The *E*-isomer is partly converted into the *Z*-isomer during synthesis.

As in the bromofluorination reactions, the expected regiospecificity and stereospecificity of the electrophilic addition of ClF to multiple bonds has been observed (cf. Table 2). Thus allyl alcohol and its derivatives are chlorofluorinated non-regiospecifically (Table 3, Nos.2–5). Derivatives of allyl alcohol give rise to 60–70% of adducts in conformity with the Markovnikov rule and to 30–40% of adducts contrary to the Markovnikov rule. The extensive migration of bromine from the allyl position to the central carbon atom [adduct (XIV), Scheme 4] has been demonstrated in relation to allyl bromide:

Scheme 4



The introduction of carbonium ion-stabilising substituents in the 2-position in the propene system (Table 3, Nos.6–9) makes the chlorofluorination reaction regiospecific and makes it conform to the Markovnikov rule:

$$CH_2{=}CHalCH_2X \xrightarrow[HF]{>NCl} CH_2ClCHalFCH_2X\ ;$$

Hal=Cl, F, X=OH, Cl .

An analogous influence of the substituents is manifested in the chlorofluorination of methyl acrylate and its α-substituted derivatives (Table 3, Nos.15–18). The chlorofluorination of *E*- and *Z*-1,3-dichloropropenes is regiospecific and to a high degree *anti*-stereoselective (93–100%) (Table 2, Nos.10 and 11). As in the bromofluorination of these alkenes, the chlorine atom at the double bond controls the mode of addition: electrophilic chlorine is directed to the central carbon atom, while the fluoride anion is directed to the terminal carbon atom. Compound Nos.19 and 21 (Table 3) show that other regioselective chlorofluorination reactions can also be *anti*-stereospecific. The electrophilic chlorofluorination of the methyl esters of *E*- and *Z*-β-chlorocrotonic acids (Table 3, Nos.22 and 23) takes place non-stereospecifically due to the cause already considered (Scheme 1).

The substitution fluorination of certain organic bromo-derivatives can be achieved with the aid of systems consisting of compounds with an active chlorine atom and anhydrous hydrogen fluoride at temperatures between −10° and +10 °C.[76] Compounds with both N–Cl and O–Cl bonds are suitable as sources of electrophilic chlorine, for example, hexachloromelamine, trichloroisocyanuric acid, and trifluoroacetyl hypochlorite:

$$-\overset{|}{\underset{|}{C}}Br + >NCl + HF \rightarrow -\overset{|}{\underset{|}{C}}F + >NH + BrCl$$

(–OCl) (–OH)

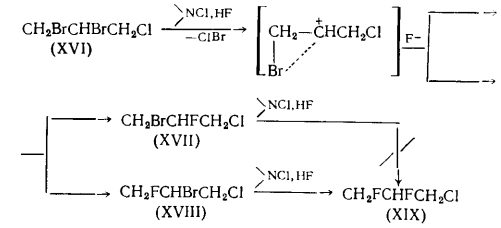
N-Bromosuccinimide does not enter into this reaction. For successful fluorination, it is essential that either the reagent or the substrate should dissolve readily in anhydrous hydrogen fluoride. The best results (yield of fluoro-derivatives 50–70%) have been obtained with polyhalogenoalkanes containing bromine atoms at a secondary or tertiary carbon atom. The substitutional fluorination of 1,2-dibromo-3-chloroisobutane by the hexachloromelamine–hydrogen fluoride system, in which one equivalent of >NCl acts on one mole of the alkane, yields exclusively 1-bromo-3-chloro-2-fluoroisobutane (XV):

$$BrCH_2\underset{Me}{C}BrCH_2Cl \xrightarrow[HF]{>NCl} \left[BrCH_2\overset{+}{\underset{Me}{C}}CH_2Cl\right] \xrightarrow{F^-} BrCH_2\underset{Me}{C}FCH_2Cl$$

(XV)

On treatment with an excess of the electrophile, the primary bromine atom in the alkane (XV) is not substituted by fluorine. Evidently, the rate-determining stage in the substitution reaction is the electrophilic debromination of the substrate with formation of an intermediate carbonium ion, which is stabilised by capturing a fluoride ion. The substitutional fluorination by these systems does not always proceed regioselectively. Vicinal dibromides can give rise to both isomeric fluoro-derivatives, probably as a consequence of the formation of bridges bromonium intermediates (Scheme 5):

Scheme 5



On treatment of 1,2-dibromo-3-chloropropane (XVI) with one equivalent of hexachloromelamine in hydrogen fluoride, a mixture of the isomeric monofluorides (XVII) and (XVIII) was obtained in proportions of 3 : 1 in an overall yield of 60%. On treatment with an excess of the electrophile, the secondary bromide (XVIII) is converted preferentially into the chlorodifluoropropane (XIX). It is evident from the examples of the substitutional fluorination reactions presented here that the chlorine atoms in the molecule are not involved.

This fact shows unambiguously that chlorine monofluoride is not formed as such in the $\rangle$NCl–HF systems. As will be shown below, ClF readily substitutes bromine in primary bromides of the type of compounds (XV) and (XVII), while in anhydrous hydrogen fluoride it substitutes chlorine in primary chloro-derivatives.

2. Chlorination with Chlorine Monofluoride

Chlorine monofluoride readily reacts with both organic and inorganic hydroxy-compounds and some of their derivatives, forming the corresponding hypochlorites in accordance with the general mechanism[77–86]

$$ROH + ClF \rightarrow ROCl + HF .$$

Such processes usually proceed extremely vigorously with evolution of much heat; the final products (hypochlorites) are explosive. Caution must therefore be exercised in carrying out these reactions: the reagent must be introduced gradually, inert solvents must be employed, and the temperature must be rigorously controlled. Chlorine nitrate,[77,78] perfluoroalkyl hypochlorites,[79–81] CF_3OOCl,[82,83] acyl hypochlorites,[84,85] and chlorine trifluoromethanesulphonate[81,86] have been synthesised in this way in high yields. The above compounds have been used in subsequent syntheses as effective electrophiles.[62] ClF reacts with water in a more complex manner, forming $ClFO_2$, Cl_2, O_2, and HF.[87]

Chlorine monofluoride chlorinates aromatic compounds—benzene, chlorobenzene, and even nitrobenzene.[88] The *o*- and *p*-derivatives have been obtained from chlorobenzene and toluene in proportions of 2 : 1, while *m*-chloronitrobenzene has been synthesised from nitrobenzene.

3. The Addition of Chlorine Monofluoride to Multiple Bonds

Chlorine monofluoride adds to the heteroatomic multiple bonds C≡N,[89] N≡S,[90] S=O,[91,92] S=N,[93] C=N,[94–97] and C=O.[79,98–100] In certain cases such addition proceeds in the absence of catalysts. For example, sulphur trioxide readily interacts with ClF, forming chlorine fluorosulphate:

$$SO_3 + ClF \rightarrow ClOSO_2F .$$

Carbonyl fluoride reacts with ClF only in the presence of catalysts—Lewis acids or bases, forming trifluoromethyl hypochlorite:

$$COF_2 + ClF \xrightarrow{CsF} CF_3OCl .$$

The fluorides of carboxylic perfluoro-acids react with ClF in the presence of CsF. It has been suggested that caesium perfluoroalkoxide is formed initially and is then converted into the corresponding hypochlorite with regeneration of CsF:

$$R_FC(=O)F + CsF \rightarrow R_FCF_2OCs ;$$
$$R_FCF_2OCs + ClF \rightarrow R_FCF_2OCl + CsF .$$

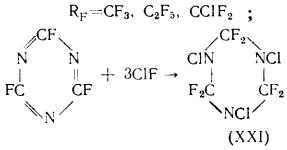
Chlorine monofluoride activated by hydrogen fluoride adds to the carbonyl group of perfluoroketones. In this case the action of the catalyst is apparently directed to ClF and not the substrate:

$$ClF + HF \rightarrow Cl^+ \rightarrow Cl^+HF_2^- ;$$
$$R_F{}_2C{=}O + Cl^+HF_2^- \rightarrow \left[R_F{}_2C^+{-}OCl\right]HF_2^- \rightarrow R_F{}_2CFOCl + HF .$$

The nitriles of carboxylic perfluoroacids and cyanuric fluoride combine with ClF via their –C≡N and C=N bonds, the corresponding adducts being formed in high yields (70 to 90%):[101,102]

$$R_FC{\equiv}N + 2ClF \xrightarrow{-78-0^\circ} R_FCF_2NCl_2 ;$$
(XX)

R_F = CF_3, C_2F_5, $CClF_2$;



(XXI)

The chlorofluoroadducts, namely the *N*-chloroamines (XX) and (XXI), are themselves mild fluorinating agents.[102] Chlorocyanogen also combines with two moles of ClF and the resulting chloroamine is dechlorinated during the reaction to give the corresponding *N*-chloroimines:[103]

$$ClCN + 2ClF \rightarrow CF_2ClNCl_2 \rightarrow CF_2{=}NCl + Cl_2 .$$

Fluorinated isocyanates readily combine with ClF at room temperature:[95]

$$R_FN{=}C{=}O + ClF \rightarrow R_FNClC(=O)F ;$$
(XXII)

R_F = CF_3, CF_3CO, FCO, Cl .

Derivatives of *N*-chlorocarbamic acid (XXII) are formed in yields of 75–90%. The fluoroketone *N*-perfluoroacylimines,[104] *N*-halogenoimines,[96] and *N*-perfluoroalkylimines[70,89,97] react analogously with ClF. Chlorine monofluoride diluted with nitrogen, under conditions where the substrate is highly diluted with an inert solvent (CCl_4, 15–20 : 1 by volume), readily adds even to butadiene and styrene.[105,106] The addition of ClF to halogeno-olefins and certain derivatives of αβ-unsaturated carboxylic acids (esters and acid chlorides) takes place in solvents (CCl_4, CCl_2FCF_2Cl, $CHCl_3$) at room temperature without preliminary dilution of the reagent with an inert gas. The chlorofluoroadducts have been obtained in satisfactory yields and in a number of instances in very high yields (50–90%).[107,108]

The regiospecificity and stereochemistry of the chlorofluorination of substituted olefins by chlorine monofluoride in a non-polar medium and in anhydrous hydrogen fluoride have been investigated (Table 4).

The mode of addition of ClF to the double bonds of substituted alkenes depends on the substituents and the medium. Vinyl chloride and trichloroethylene are chlorofluorinated in Freon-113 in conformity with the Markovnikov rule (Table 4, Nos.1 and 4). The chlorofluorination of vinylidene chloride under the same conditions gives rise to 12% of the adduct formed contrary to the Markovnikov rule (Table 4, No.3) and is to a large extent accompanied by the elimination of a proton and the formation of trichloroethylene:

$$CH_2{=}CCl_2 \xrightarrow[\text{Freon, } 20-30^\circ]{ClF} \left[CH_2{-}\overset{+}{C}Cl_2 \leftrightarrow CH_2{=}CCl_2{}^+\right] \xrightarrow{F^-} CH_2ClCCl_2F + CH_2FCCl_3 ;$$
$$\xrightarrow{-H^+} CHCl{=}CCl_2 .$$

The chlorofluorination of allyl derivatives both in a non-polar medium and in hydrogen fluoride takes place non-regiospecifically (Table 4, Nos.6–10): adducts formed in conformity with the Markovnikov rule predominate in the mixture of isomers (60–70%) regardless of the type of allyl substituent.

Table 4. The regiospecificity and stereochemistry of the chlorofluorination of substituted alkenes by an equimolar amount of chlorine monofluoride (reaction carried out in $CHCl_3$ or $CF_2ClCFCl_2$*; the data for the reaction in HF are given in brackets**).

No.	Initial alkene	Regiospecificity, %		Stereospecificity, %	Refs.
		$C^1(Cl)-C^2(F)$	$C^1(F)-C^2(Cl)$		
1	$C^1H_2=C^2HCl$ ***	100	0	—	[105]
2	$CHCl=CHCl$ ***	—	—	—	[105, 108]
3	$C^1H_2=C^2Cl_2$ ***	88	12	—	[108]
4	$C^1HCl=C^2Cl_2$ ***	100	0	—	[88, 108]
5	$CCl_2=CCl_2$ ***	—	—	—	[108]
6	$C^1H_2=C^2HCH_2Cl$ ***	57	43	—	[88, 108]
7	$C^1H_2=C^2HCH_2Br$ ***	55	45	—	[108]
8	$C^1H_2=C^2HCH_2OCHO$	64 (75)	36 (25)	—	[107]
9	$C^1H_2=C^2HCH_2OCOOMe$	60 (68)	40 (32)	—	[107]
10	$C^1H_2=C^2HCH_2OCOCCl_3$	60	40	—	[107]
11	Z-$C^1HCl=C^2HCH_2Cl$ ***	2	98	90	[107, 108]
12	E-$C^1HCl=C^2HCH_2Cl$ ***	20	80	90	[107, 108]
13	$C^1H_2=C^2HCCl_3$ ***	0	100	—	[108]
14	$CF_2=CFCF_3$ ***	0	100	—	[108, 109]
15	E-$CF_3CF=CFCF(CF_3)_2$	Does not react		—	[108]
16	$C^1H_2=C^2HCOOMe$	30 (9)	70 (91)	—	[107]
17	$C^1H_2=C^2(Me)COOMe$	53 (95)	47 (5)	—	[107]
18	$C^1H_2=C^2(Me)COCl$	35	65	—	[107]
19	Z-$C^1HCl=C^2FCOOMe$	22 (0)	78 (100)	50 (100)	[107, 108]
20	Z-$C^1HF=C^2FCOOMe$	—	—	—	[108]
21	$C^1F_2=C^2(CF_3)COOMe$	0 (0)	100 (100)	—	[108]
22	Z-$C^1Cl(Me)=C^2HCOOEt$	(0)	(100)	—	[107]
23	E-$C^1Cl(Me)=C^2HCOOEt$	(0)	(100)	—	[107]
24	Z-$CH(COOMe)=CHCOOMe$	—	—	100 (100)	[107]
25	E-$CH(COOMe)=CHCOOMe$	—	—	100 (100)	[107]
26	Z-$C^1H(COOMe)=C^2ClCOOMe$ ****	100 (100)	0	2:1 (1:4)*****	[108]
27	E-$CH(COOMe)=CClCOOMe$ ****	100 (100)	0	1:4 (1:1)*****	[108]
28	$C^1Cl(COOMe)=C^2FCOOMe$ ****	40 (10)	60 (90)	15:1 (1:8)*****	[108]

*15% (by volume) of alkene in chloroform or Freon.

**50% (by volume) of alkene in anhydrous HF.

***The halogenoalkenes are insoluble in liquid HF and their chlorofluorination in this medium was not therefore investigated.

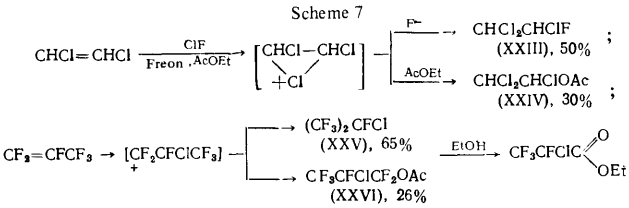
****A 2–10-fold excess of ClF was passed into a solution of the alkene in Freon.

*****The reaction is non-stereospecific and the configuration of the diastereoisomeric adducts was not determined. The ratio of the diastereoisomers is given; it is seen from the figures quoted that one diastereoisomer predominates in a non-polar medium and the other in hydrogen fluoride.

The chlorofluorination of allyl bromide involves the migration of bromine from the allyl position to the central carbon atom; the ratio of the regioisomers (XII)–(XIV) is the same as in the coupled chlorofluorination by the hexachloromelamine–hydrogen fluoride system (see Scheme 4). The addition of ClF to Z- and E-1,3-dichloropropenes (Table 4, Nos.11 and 12) takes place regioselectively (98% of the Z-isomer and 80% of the E-isomer, in contrast to the complete regiospecificity in the coupled chlorofluorination of these olefins—cf. Nos.10 and 11 in Table 3) and *anti*-stereoselectively.

The electrophilic mechanism of the chlorofluorination of polyhalogenoalkenes, including tetrachloroethylene and perfluoropropene, by chlorine monofluoride in non-polar media has been confirmed by the involvement of an external nucleophile—ethyl acetate:[10] the chlorofluorination of dichloroethylene and perfluoropropene in Freon in the presence of ethyl acetate afforded up to 30% of the acetates (XXIV) and (XXVI) together with the chlorofluoroadducts (XXIII) and (XXV) (Scheme 7):

Scheme 7



The regio- and stereo-specificities are markedly different in the reactions of the esters of αβ-unsaturated carboxylic acids with ClF in a non-polar medium and in liquid hydrogen fluoride (Table 4, Nos.16–28). Methyl acrylate (Table 4, No.16) gives rise to regioisomers in proportions of 1 : 2.5 in $CHCl_3$ and 1 : 10 in HF, while for methyl methacrylate (Table 4, No.19) the corresponding ratios are 1 : 1 and 19 : 1. Nevertheless, these unsaturated compounds react with ClF via an electrophilic mechanism in both media: the reactions are extremely fast and, together with chlorofluoroadducts, give rise to products resulting from the involvement of the external nucleophile—acyloxychloroadducts.[107]

Dimethyl maleate and dimethyl fumarate readily combine with ClF in both $CHCl_3$ and HF. The addition takes place *anti*-stereospecifically in both media, which also indicates an electrophilic mechanism.

The esters of αβ-unsaturated acids containing more than two electron-accepting substituents at the multiple bond are smoothly chlorofluorinated only by the ClF–HF system (Table 4, Nos.20–23 and 26–28). The reactions in the instances investigated have been non-stereospecific. In order to complete the reactions of unsaturated esters containing electron-deficient multiple bonds, an excess of the reagent is required in a non-polar medium and the stereochemical result is completely different from that in HF (Table 4, Nos.26–28).

Chlorine monofluoride activated by hydrogen fluoride is an extremely effective electrophilic addend. No multiple bonds incapable of homophase chlorofluorination by this system for electronic or steric reasons have been found. Methyl perfluoromethacrylate, for which no electrophilic addition reactions had been known,[110] interacts smoothly with the stoichiometric amount of ClF in hydrogen fluoride.

4. Substitution of the Halogens in Organic Halogenoderivatives by Fluorine

Chlorine monofluoride is an active agent for the selective substitutional fluorination of bromoalkanes and bromoesters. The reaction takes place when a stoichiometric amount of gaseous ClF is passed through a liquid bromoalkane or a solution of a bromoalkane in a suitable inert solvent (CCl_4, $CFCl_2$, $CFCl_2$) at temperatures between −50° and 50 °C.[111,112] Under these conditions, the chlorine atoms and alkoxycarbonyl groups in the substrate molecule are not involved. The yields are exceptionally high in most cases. Chlorine monofluoride abstracts a bromide anion from the organic substrate with formation of bromine monochloride and the

corresponding carbonium ion, which is stabilised by capturing a fluoride anion:

$$RBr + ClF \rightarrow ClBr + [R^+] \xrightarrow{F^-} RF .$$

The bromine monochloride evolved makes the reaction conditions milder, diminishing the risk of combustion of the polyhydro-substrate on contact with ClF. Naturally, for this mechanism of the substitution of bromine by fluorine, the usual bromide reactivity series is observed: tertiary > secondary > primary.

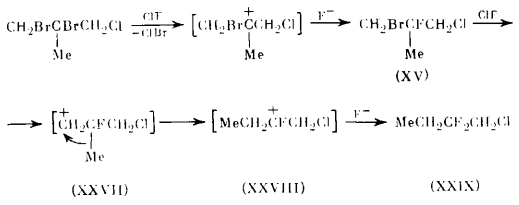
The most favourable conditions for the substitutional fluorination of bromo-derivatives obtain at temperatures in excess of 0–10 °C. At these temperatures, chlorine monofluoride debrominates almost any bromo-derivative with the exception of compounds of the type of R_FCF_2Br and RCHBrCOOR'.

At low temperatures (between −20° and −50 °C) in the case of unreactive substrates, the bromine monochloride evolved enters into a competing reaction with ClF, forming bromine trifluoride (T_m = 9 °C), which is frozen out from the reaction mixture. On fusion, BrF_3 reacts vigorously with the substrate. The reaction becomes uncontrollably explosive even with CCl_4. At temperatures in the range 20–40 °C almost the entire bromo-derivative reacts with ClF smoothly and selectively, giving rise to the corresponding fluorides.[112]

The high selectivity of the substitutional fluorination can be seen from the following example (Scheme 8).

When 1,2-dibromo-3-chloroisobutane is acted upon by one mole of ClF, the tertiary fluoride (XV) is formed regioselectively; the abstraction of the primary bromine atom on treatment with a second mole of ClF also takes place readily and is accompanied by the migration of the methyl group in the carbonium ion (XXVII). This results in the formation of the more stable α-fluorocarbonium ion (XXVIII), which captures a fluoride anion and gives rise to the geminal difluoride (XXIX):

Scheme 8

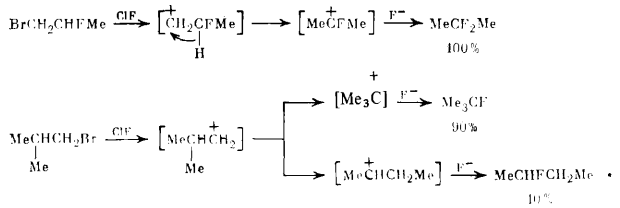


(XXVII) (XXVIII) (XXIX)

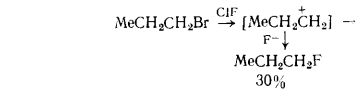
It is seen from this example to what extent gaseous ClF in a non-polar medium is a stronger electrophile than hexachloromelamine in hydrogen fluoride. The latter is incapable of abstracting a primary bromine atom from the halogenoalkane (XV) (see above). The debromination of the primary bromides is accompanied in most cases by the migration of the vicinal substituents—methyl groups and chlorine atoms. 1-Bromo-2-chloropropane (XXX) is readily fluorinated with migration of a chlorine atom. The primary bromoalkanes (XXX) and the isomeric secondary bromoalkane (XXXI) therefore give rise to the same fluorination product—1-chloro-2-fluoropropane (XXXII):

$$\underset{\text{(XXX)}}{MeCHClCH_2Br} \xrightarrow{ClF} \underset{\text{(XXXII)}}{MeCHFCH_2Cl} \xleftarrow{ClF} \underset{\text{(XXXI)}}{MeCHBrCH_2Cl} .$$

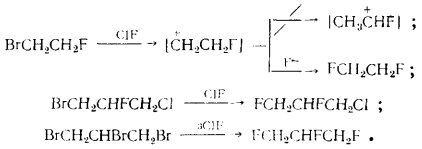
The driving force of all the migrations observed in substitutional fluorination is the formation of a stable carbonium ion. If migration can produce a stable tertiary carbonium ion, then a hydride shift takes place even in a non-polar medium:



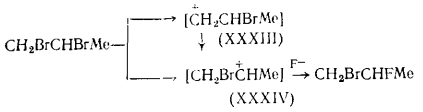
In the fluorination of n-propyl bromide in Freon-113 at 0–10 °C the debromination of the substrate is also accompanied by a hydride shift, but 1-fluoropropane is formed together with 2-fluoropropane:



Primary fluorides can be obtained in non-polar media in all cases where the alternative hydride shift would have led to an insufficiently stable carbonium ion:[111,112]



Comparison of the relative rates of fluorination of n-propyl and isopropyl bromides showed that the difference between their reactivities is small (1 : 2).[112] Nevertheless 1,2-dibromopropane reacts selectively with one mole of ClF to form 1-bromo-2-fluoropropane:



Bearing in mind the tendency of the halogens (Br, Cl) to migrate, it is understandable why the primary cation (XXIII) formed on debromination rearranges to the more stable secondary cation (XXXIV), which in fact accounts for the high selectivity of the substitution.

A study of the relative rates of the substitutional fluorination of bromoalkanes in non-polar media by the method of competing reactions[112] established that the vicinal halogens very greatly retard the fluorination reaction. The following sequence of reactivities has been observed for secondary bromides:

$$MeCHBrMe \gg MeCHBrCH_2Cl \gg ClCH_2CHBrCH_2Cl .$$

Analogously for primary bromides, we have

$$EtCH_2Br \gg MeCHClCH_2Br .$$

The geminal halogen atoms retard the fluorination reaction only very slightly. Thus ethyl bromide and 1-bromo-1-chloroethane are fluorinated at approximately equal rates, while in the series of dibromoethanes the following ratios of the rates of fluorination have been observed:

$$BrCH_2CH_2Br : BrCH_2CHClBr : BrCH_2CCl_2Br = 10 : 3 : 1 .$$

α-Halogenofluorides are formed exclusively under these conditions on reaction with a stoichiometric amount of ClF:

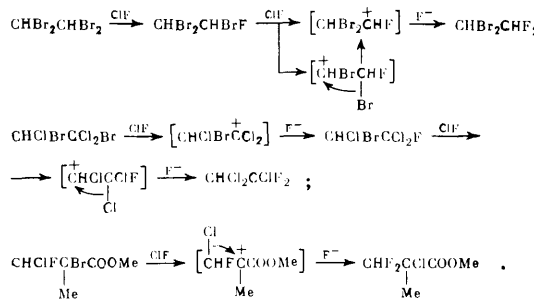
$$\underset{\text{(XXXV)}}{BrCH_2CHClBr} \xrightarrow{ClF} [BrCH_2\overset{+}{C}HCl] \xrightarrow{F^-} BrCH_2CHClF .$$

Such high selectivity is associated with the fact that, for example, in compound (XXXV) the bromine atom in the CH_2Br group is deactivated by the two vicinal halogens to

a much greater extent than the bromine atom of the CHClBr group is deactivated by one geminal and one vicinal halogen atom.

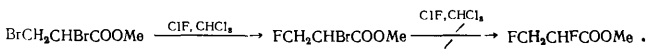
For the same reason, MeCHClBr is fluorinated incomparably faster than $ClCH_2CH_2Br$. Since the halogen atoms are distinguished by dual electronic properties, i.e. exhibit negative inductive and positive resonance effects, the resonance delocalisation of the positive charge of the α-halogenocarbonium ion is in all probability manifested already in the transition state of the debromination reaction, while the vicinal halogens do not show an anchimeric cooperation with the electrophilic dehalogenation.

The fluorine atoms exhibit a high resonance effect and do not tend to migrate, so that the substitutional fluorination of vicinal dibromoalkanes and polybromoalkanes leads to geminal difluorides:

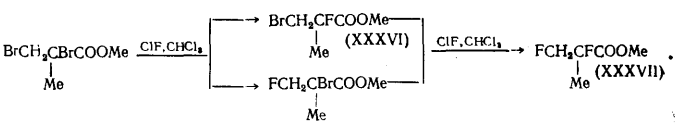


A high selectivity is probably not to be expected in the fluorination of bromoalkanes where the CH_2Br and CHHalBr (or $CHal_2Br$) groups are located in positions more remote than the vicinal position.

The ester group deactivates the bromine atom in the α-position. Methyl αβ-dibromopropionate reacts with ClF in a non-polar medium to form the product of the substitution mainly of the β-bromine atom:[111]



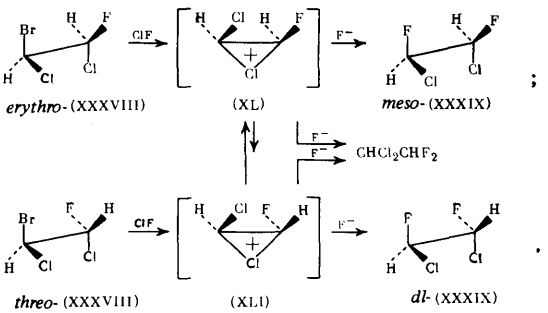
The introduction in the α-position of a substituent stabilising carbonium ions activates the α-halogen. For this reason, methyl αβ-dibromoisobutyrate reacts with one mole of ClF to form a mixture of the α-fluoro- and β-fluoro-regioisomers in proportions of 3 : 1, while treatment of the same mixture with a further mole of ClF results in the formation of methyl αβ-difluoroisobutyrate (XXXVII):



It is striking that in a non-polar medium the methyl group does not migrate on debromination of the primary bromide (XXXVI), while the debromination of the same compound in hydrogen fluoride entails the migration of the methyl group and the formation of the geminal difluoride, namely methyl αα-difluorobutyrate, and not the vicinal difluoride (XXXVII).[76] It is to be expected that the substitutional fluorination reactions proceeding via the dehalogenation stage will exhibit a low selectivity.

The fluorination of *erythro*- and *threo*-1-bromo-1,2-dichloro-2-fluoroethanes (XXXVIII) by chlorine monofluoride in the absence of a solvent proceeds non-stereospecifically[111] (Scheme 9). Mainly *meso*-1,2-dichloro-1,2-difluoroethane (XXXIX) (85% in a mixture of diastereoisomers) is formed from the *erythro*-isomer of compound (XXXVIII), while the *threo*-isomer gives rise to a mixture of equal amounts of the *meso*- and *dl*-isomers of compound (XXXIX).

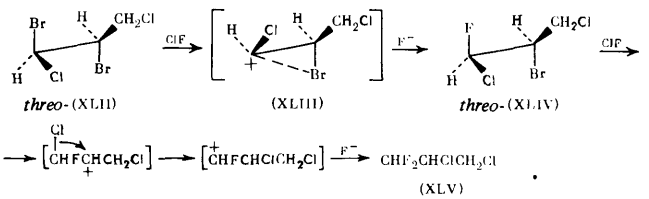
Scheme 9



The preferential retention of the configuration in the case of the *erythro*-isomer of compound (XXXVIII) is probably to be accounted for by the stabilisation of the intermediate carbonium ion (XL) by the interaction of the cisoid chlorine and fluorine atoms (cf. Section III above); in the case of the *threo*-isomer of compound (XXXVIII) there is no such stabilisation in the carbonium ion (XLI) and the reaction is non-stereoselective.

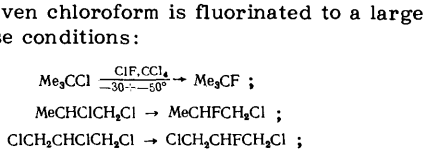
The substitutional fluorination of *erythro*- and *threo*-1,2-dibromo-1,3-dichloropropanes (XLII) takes place regiospecifically at the terminal bromine atom and mainly (85–90%) with retention of the configuration, which can probably be accounted for by the formation of the bromonium ion (XLIII) as a result of the involvement of the neighbouring bromine atom maintaining the configuration of the carbonium ion (Scheme 10):

Scheme 10



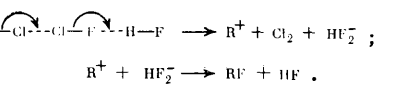
On treatment of 2-bromo-1,3-dichloro-1-fluoropropane (XLIV) with a second mole of ClF, the debromination is accompanied by the migration of a chlorine atom and the only fluorination product is therefore the geminal difluoride (XLV).

In the absence of special catalysts, chlorine monofluoride can substitute the chlorine atoms by fluorine in compounds which give rise to fairly stable carbonium ions following the elimination of Cl^-.[113] Reactions of this kind occur when ClF is passed into the corresponding substrate or its solution in an inert solvent at temperatures between −50° and −10 °C. t-Butyl chloride, 1,2-dichloropropane, and 1,2,3-trichloropropane are readily fluorinated in this way in nearly quantitative yields. Even chloroform is fluorinated to a large extent under these conditions:

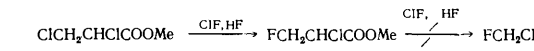


The examples quoted demonstrate the high selectivity of the fluorination reaction: the primary chlorine atoms are not involved. For a more far-reaching fluorination, ClF must be activated by hydrogen fluoride or Lewis acids.[113]

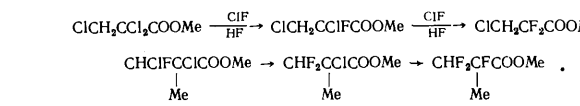
In anhydrous hydrogen fluoride, chlorine monofluoride readily substitutes the chlorine in organic chloro-derivatives by fluorine at temperatures between −60° and 10 °C. The reaction proceeds readily when gaseous ClF is passed into a solution or a stirred emulsion of the chloro-derivative in hydrogen fluoride:



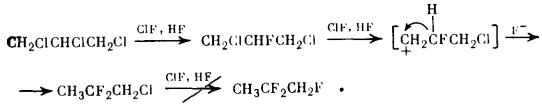
The reaction suffers from the same limitation as the substitution of bromine by fluorine: the chlorine atom of the CHCl group in the α-position relative to the alkoxycarbonyl group is not substituted. When one mole of methyl dichloropropanoate is treated with one mole of ClF, only the β-chlorine atom is substituted:



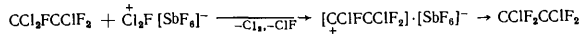
When a second mole of ClF is passed in, the chlorine atom in the α-position is not involved and the electrophilic attack by ClF is directed to the oxygen atom of the carbonyl group (see below). The introduction in the α-position of substituents stabilising carbonium ions promotes the substitution of the α-chlorine atom by fluorine:



Hydrogen fluoride used as a medium in substitutional fluorination promotes hydride shifts with formation of more stable carbonium ions. When 1,2,3-trichloropropane interacts with one mole of ClF, the central chlorine atom is substituted selectively and subsequent attack on the primary chlorine atom in 1,3-dichloro-2-fluoropropane is accompanied by a hydride shift, which results in the formation of a single product—1-chloro-2,2-difluoropropane, whose chlorine atom is not subsequently substituted under these conditions:

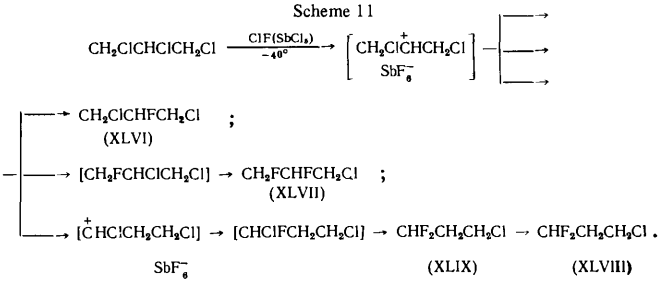


Catalytic amounts of antimony(V) halides (3–5%) enhance the fluorinating activity of chlorine monofluoride in a non-polar medium,[113] which can probably be accounted for by the formation of dichlorofluoronium hexafluoroantimonate,[114] in which the electrophilic activity of the chlorine is so high that the complex is capable of fluorinating Freon-113 to Freon-114 at temperatures between −40° and −60 °C.



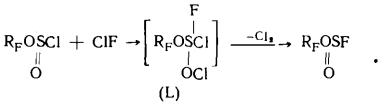
The substitutional fluorination by chlorine monofluoride catalysed by antimony salts is less selective than the fluorination in the absence of a catalyst or using the ClF–HF system. Thus considerable amounts of 3-chloro-1,2-difluoropropane (XLVII), 3-chloro-1,1-difluoropropane (XLVIII), 3-chloro-1,1-difluoropropane (XLIX), and 1,1,3-trifluoropropane (XLIX) have been obtained together with the main product, namely 1,3-dichloro-2-fluoropropane (XLVI), from 1,2,3-trichloropropane by its reaction with an equimolar amount of ClF in the presence of 5% $SbCl_5$ (Scheme 11):

Scheme 11



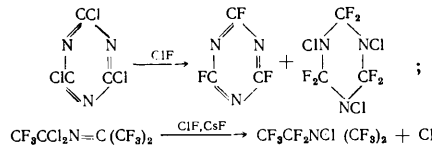
Fluorination by chlorine monofluoride thus has extensive preparative possibilities for the specific synthesis of various mono- and poly-fluorides by varying the temperature of the reaction and the catalytic additives.

Chlorine monofluoride is capable of substituting also the chlorine of acid chlorides in perfluoroalkyl chlorosulphites:[115]



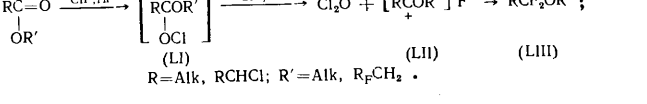
Since such substitution does not occur on treatment with alkali metal fluorides at high temperatures, presumably the reaction proceeds via the electrophilic addition of ClF to the S=O group and subsequent dechlorination of the hypochlorite (L).

It has been suggested that the analogous chlorofluorination with subsequent dechlorination takes place on fluorination of cyanuric chloride, hexachloromelamine,[116] hexachlorobutadiene,[117] and certain chlorine-containing polyfluoroalkylimines[89] by chlorine monofluoride:



5. The Conversion of the Carbonyl Group into the Difluoromethylene Group

When chlorine monofluoride is allowed to react with a solution of an ester in anhydrous hydrogen fluoride at temperatures from −70° to −20 °C, the oxygen of the carbonyl group is smoothly substituted with formation of the difluoromethylene group.[118] The familiar reaction involving the addition to ClF to the carbonyl group probably takes place initially with formation of the hypochlorite (LI) (see above). On further interaction with ClF, the electrophilic elimination of the ClO group probably takes place and the stable carbonium ion (LII) is formed. The latter captures a fluoride anion and is converted into the αα-difluoroether (LIII):



The requirements for the stability of the intermediate ion (LII) are so stringent that the introduction of two electron-accepting substituents in the α-position relative to the carbonyl group prevents the reaction. For example, the RCF_2COO group cannot be converted under these conditions into RCF_2CF_2O. Since many examples of compounds of type (LIII), such as, for example, $MeCF_2OCH_2CF_2CF_2H$ are

hydrolytically unstable, in their isolation from the reaction system it is necessary to avoid contact with water. Fluoroethers, for example, $ClCH_2CF_2OCH_2CF_2CF_2H$, which are potential anaesthetics and are fairly resistant to hydrolysis can be synthesised in this way.[119]

When the ethyl esters of acids are used as substrates, more far-reaching fluorination is observed. On treatment with three moles of ClF, ethyl chloroacetate gives rise to a high yield of 1-chloro-2,2,4-trifluoro-3-oxapentane:

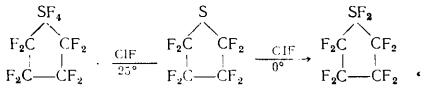
$$ClCH_2COOCH_2Me \xrightarrow[HF]{3ClF} ClCH_2CF_2OCHFMe\ .$$

6. Oxidative Fluorination of Sulphur-containing Compounds

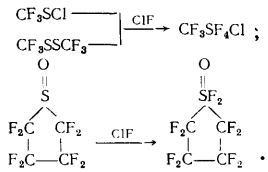
Chlorine monofluoride readily effects the successive oxidation of sulphur(II) to sulphur(IV) and sulphur(VI). Reactions of this kind have been thoroughly investigated in relation to perfluorinated sulphur-containing compounds and have been discussed in reviews.[62,120] We shall therefore quote only certain examples of such reactions achieved with high yields of the products. Perfluoroalkyl sulphides react smoothly with ClF at −78 °C, forming *SS*-difluorides, while at a higher temperature further oxidation of sulphur(IV) to sulphur(VI), accompanied by the partial dissociation of the C–S bonds, takes place:

$$R_FSR'_F \xrightarrow[-78°]{ClF} R_FSF_2R'_F\ ;$$

$$CF_3SCF_3 \xrightarrow[20°]{ClF} CF_3SF_4CF_3 + CF_3SF_4Cl\ ;$$



Perfluoroalkanesulphenyl chlorides, disulphides, and sulphoxides are also readily oxidised and fluorinated under mild conditions:



7. Chlorine Monofluoride as a Member of the Series of Fluorine-containing Reagents with Electrophilic Halogens

The reactions considered show that chlorine monofluoride is a typical electrophile, the majority of the reactions of which with organic substrates proceed via polar mechanisms, thoroughly investigated in organic chemistry, with formation of carbonium ion intermediates. On the whole, the observed facts (the mode of addition to multiple bonds as a function of the electronic nature of the substituents and the medium, the stereochemistry of the addition and substitution, and the skeletal rearrangements and migrations accompanying these reactions in non-polar and polar media or in the presence of antimony salts) are consistent with the predictions based on the extensive experience gained in the chemistry of carbonium ions. The observed specific features in individual reactions are not of fundamental importance, reflecting merely the influence of the medium, the counterion, and the neighbouring groups on the stability of the carbonium ions.

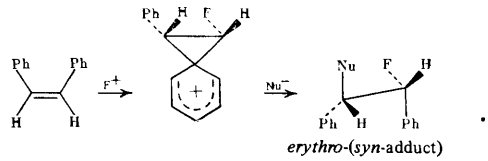
In contrast to other halogens, ClF does not tend to undergo homolytic reactions at the usual temperatures and, as a consequence of the considerable polarity of its bond (μ = 0.89 D), it adds via an electrophilic mechanism even to polyhalogenoalkenes in non-polar solvents, which implies that its reactivity is close to that of a powerful electrophile such as chlorine fluorosulphate.[121–125]

The high selectivity of ClF as a reagent and as a consequence the great preparative scope of its application in the synthesis of a wide variety of mono- and poly-fluorides proved to be somewhat unexpected. The majority of the related reagents containing an electrophilic halogen, namely chlorine and bromine fluorosulphates $FSO_2OCl(Br)$,[121–125] chlorine and bromine trifluoromethanesulphonates CF_3SO_2OCl. .(Br),[127–130] chlorine perchlorate ClO_3OCl,[131,132] perfluoroalkyl hypochlorites and hypofluorites $R_FOCl(F)$,[133–135] and perfluoroacyl hypochlorites and hypofluorites,[136–138] have been used for preparative purposes mainly in reactions with polyhalogeno- and perfluoro-compounds. Reactions involving electrophilic addition to multiple bonds and electrophilic debromination and dechlorination of organic halogeno-derivatives with formation of carbonium ions, which are stabilised by capturing the corresponding nucleophilic residue, are characteristic of these reagents as well as chlorine monofluoride. Polyfluoroalkyl fluorosulphates, trifluoromethanesulphonates, perchlorates, perfluoroalkyl ethers, and perfluoroacylates have been obtained with the aid of these reactions. It has been shown that even molecular fluorine is capable of adding at −78 °C to certain alkenes in Freons 11 and 12 via an electrophilic mechanism.[139]

The electrophiles enumerated have been investigated in reactions with a limited number of substrates and under different conditions, so that it is difficult to set up an electrophile reactivity series which includes also ClF. Nevertheless, presumably chlorine fluorosulphate, chlorine trifluoromethanesulphone, and chlorine perchlorate are stronger electrophiles than ClF. Thus chlorine fluorosulphate is capable of abstracting a chloride anion, in the absence of special catalysts at temperatures below 0 °C, from dichloroethane[123] and methyl chloroacetate;[140] chlorine perchlorate and trifluoromethanesulphonate debrominate compounds of the type R_FCF_2Br,[129,132] while chlorine monofluoride does not react with compounds of this kind under the conditions indicated.

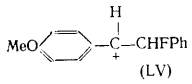
Comparison of the stereochemistries of the addition of electrophiles containing the O–Cl and O–F bonds and of chlorine monofluoride to unsaturated compounds merits attention. The *cis*- and *trans*-isomers of stilbene give rise preferentially to *syn*-adducts on reaction with reagents containing electrophilic fluorine: CF_3OF (70–80%),[136] CF_3CF_2OF (83),[134] CF_3COOF (100%).[137] The configurations of *erythro*- and *threo*-PhCHXCHFPh (X = CF_3O, CF_3CF_2O, or CF_3COO) in the studies quoted have been demonstrated reliably by NMR and do not give rise to any doubts.

The most convincing explanation of the causes of the *syn*-addition of these reagents to stilbenes is that the carbonium ion formed as a result of the electrophilic attack by fluorine is in essence a phenonium ion (LIV) as a result of the involvement of the neighbouring phenyl group, and the subsequent nucleophilic attack by this ion can lead only to the *syn*-adduct:[134,136,137]



erythro-(*syn*-adduct)

The entering fluorine atom, which behaves as a relatively ineffective neighbouring group, cannot compete with the phenyl substituent as regards its capacity to form a bridged cation. The introduction of electron-donating substituents in one of the aromatic rings of stilbene decreases the *syn*-stereospecificity of the electrophilic fluorination. since the intermediate under these conditions is the open-chain carbonium ion (LV), the attack on which by the nucleophile



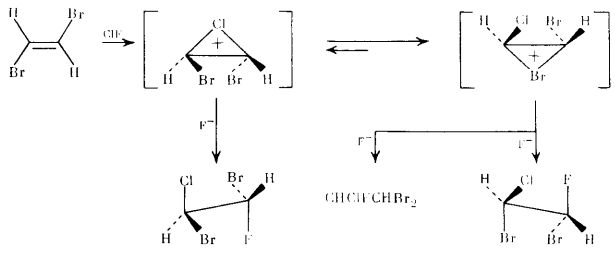
(LV)

is equally probable on either side. The stereochemistry of the addition of these electrophiles to aliphatic olefins has not been investigated but a study has been made of the addition of chlorine and bromine trifluoromethanesulphonates to *cis*- and *trans*-difluoroethylenes and also to *trans*-dichloroethylene.[128] The complete stereospecificity of the addition reaction has been demonstrated: only one diastereoisomer has been obtained from each olefin. The NMR spectroscopic parameters have been calculated for the adducts obtained [*erythro*- and *threo*-$CF_3SO_2OCHFCHFCL$ (LVI) and also for the single diastereoisomer $CF_3SO_2OCHClCHClBr$]. It has been shown that the diastereoisomeric 2-chloro-1,2-difluoroethyl trifluoromethanesulphonates (LVI) have significantly different vicinal spin–spin coupling constants $^3J_{FF} = 19.5$ and 25.5 Hz. Tentative examination of the conformations of each diastereoisomer led to the assignment of their configurations: J_{FF} = 25.5 Hz and 19.5 Hz have been assigned to the *threo*- and *erythro*-isomers of compound (LVI). The assignment of the configurations of the esters (LVI) as *syn*-adducts and also the proposed mechanism involving a concerted *syn*-addition of chlorine and bromine trifluoromethanesulphonates to 1,2-dihalogeno-ethylenes[128] appear to be extremly doubtful.

Indeed it has been established[107] that ClF, which is a less effective electrophile, adds to similar unsaturated compounds via a two-stage electrophilic mechanism with the preferential formation of *anti*-adducts (cf. Table 4). Furthermore, it has been shown[111,141] that the constants $^3J_{FF}$ for the diastereoisomeric alkanes *dl*- and *meso*-CHClFCHClF are respectively 20.8 and 26.2 Hz, while those for *dl*- and *meso*-$(CHFCOOMe)_2$ are 9.1 and 13.9 Hz. Thus the character of the variation of the constants $^3J_{FF}$ as a function of the configuration is the opposite to that proposed for *threo*- and *erythro*-(LVI).[128]

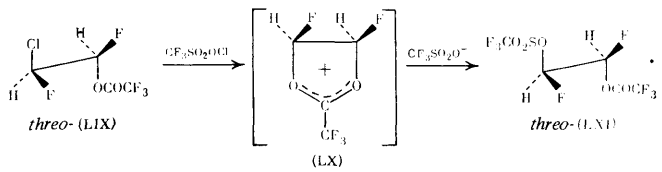
If the substrate molecule contains substituents which compete with the leaving halogen atom for the carbonium ion centre, like the phenyl substituent in stilbenes, then the electrophilic addition of ClF to such substrates involves the formation of *syn*-adducts together with the *anti*-adducts.[142] The involvement of bromine atoms in the chlorofluorination of *Z*- and *E*-1,2-dibromoethylenes is so great that in the chlorofluorination of the *E*-olefin by the hexachloromelamine–hydrogen fluoride system mainly the regioisomer (LVIII) is formed together with the pseudo-*syn*-adduct, namely *threo*-(LVII) (90 and 10% in the mixture of isomers—Scheme 12). The chlorination of this alkene by chlorine monofluoride in Freon-113 proceeds non-regioselectively and non-stereoselectively, but the pseudo-*syn*-adduct, i.e. *threo*-(LVII), predominates in the mixture of isomers.

Scheme 12



	erythro-(LVII) (*anti*-)	(LVIII)(regio-)	*threo*-(LVII) (pseudo-*syn*-)
Hexafluoromelamine-HF	<1%	90%	10%
ClF-Freon-113	15%	17%	68%

It is therefore doubtful if the addition of chlorine and bromine trifluoromethanesulphonates to 1,2-difluoro- and 1,2-dichloro-ethylenes[128] involves stereospecific *syn*-addition, because the entering halogens are more effective neighbouring groups than the substituents already present in the alkene molecules. The substitution of the chlorine atoms by the trifluoromethanesulphonate group on treatment of *erythro*- and *threo*-2-chloro-1,2-difluoroethyl-1-trifluoroacetates (LIX) with chlorine trifluoromethanesulphonate probably does indeed take place with retention of the configuration[129] but not as a consequence of cyclic synchronous substitution, the real reason being that the trifluoroacetate group present in the molecules of compound (LIX) maintains the configuration of the carbonium ion (LX):



threo-(LIX) (LX) *threo*-(LXI)

It is to be expected that in the absence from the substrate of neighbouring groups maintaining the configuration of the carbonium ion, the substitution of the halogens by the trifluoromethanesulphonate group will proceed non-stereospecifically (cf. subsection 4 above).

Reactions involving the electrophilic elimination of the halogen are characteristic not only of the heteroatomic reagents with electrophilic halogens mentioned above but also of molecular chlorine, bromine, and iodine monochloride in their interactions with alkyl iodides in inert salts at temperatures between −78° and 25 °C:[143–145]

$$RI + Hal_2 \xrightarrow{-78^\circ} RHal + IHal;$$
$$Hal = Br, Cl.$$

The reaction is preceded by the formation of a complex between the alkyl iodide and the halogen, the decomposition of which results in the formation of a carbonium ion, which captures a halide anion. The typical carbonium ion rearrangements accompanying the substitution reaction confirm this mechanism. It has been shown in relation to the reaction of the optically active 2-iodo-octane with Br_2 and Cl_2 that the substitution takes place preferentially with inversion of the configuration.[143]

V. FLUORINATION BY HALOGEN POLYFLUORIDES AND THEIR INORGANIC COMPLEXES

Halogen polyfluorides are extremely dangerous to handle.[1-4] Chlorine trifluoride ignites wood, plastics, and even concrete and gives rise to an explosion on contact with the usual organic solvents at −100 °C.[146] Bromine trifluoride is somewhat less dangerous. Nevertheless, at the usual temperatures, it reacts explosively even with chlorocarbons. Iodine pentafluoride is not quite so reactive. Only highly fluorinated Freons can be mixed safely with halogen polyfluorides at moderate temperatures. Numerous attempts to employ halogen polyfluorides for the specific synthesis of organic fluorides have led investigators to the conclusion that a common disadvantage of all these reagents is that they are completely non-selective and give rise to a very complex mixture of products.[1,2,147] For some time, this reduced the interest in halogen polyfluorides. However, in subsequent years halogen polyfluorides and their complexes have again attracted attention as fluorinating agents.

Methods of synthesis in high yields of *N*-bromoperfluoropiperidine[148] by treating trichlorohexafluoropiperidine with BrF_3 at −50 °C and also of isomeric octabromotetrafluorocyclohexanes $C_6F_8Br_4$ by treating hexabromobenzene with ClF_3, IF_5, or IF_7 in bromine at temperatures between −10° and 60 °C have been patented.[149] When certain nitriles were treated with BrF_3 in anhydrous hydrogen fluoride at temperatures between −20° and −15 °C, the corresponding trifluoromethylalkanes were obtained in high yields.[150] 2,2-Difluoropropane has been obtained from acetone under the same conditions (93%):

$$RCN + BrF_3 \xrightarrow{HF} RCF_3 ;$$
$$R=Me,\ Et,\ CH_2Cl ;$$
$$MeCOMe + BrF_3 \xrightarrow{HF} MeCF_2Me .$$

Ethyl methyl ketone and isopropyl methyl ketone reacts with bromine trifluoride in hydrogen fluoride with dissociation of the carbon chain. On treatment of perfluoroalkyl iodides with chlorine or bromine trifluoride, bromine pentafluoride, and elemental fluorine in perfluorohexane or in the absence of solvents at temperatures between −60° and −80 °C, perfluoroalkyl iodide difluorides and tetrafluorides were obtained. The conditions of the synthesis and the properties of the products have been described in detail.[146] Iodine pentafluoride is ineffective in this reaction, while the reaction with ClF_3 proceeds in accordance with the equations

$$3R_FI + 2ClF_3 \rightarrow 3R_FIF_2 + Cl_2 ;$$
$$3R_FI + 4ClF_3 \rightarrow 3R_FIF_4 + 2Cl_2 ;$$
$$R_F=C_2F_5,\ C_4F_9,\ C_6F_{13},\ C_{10}F_2 .$$

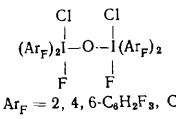
When elemental fluorine is used, three products are formed simultaneously:

$$C_4F_9I + F_2 \rightarrow C_4F_9IF_2 + C_4F_9IF_4 + (C_4F_9)_2I^+IF_6^- .$$

Freshly prepared perfluoroalkyl iodide difluorides are slow-melting solids; on standing, they are converted into insoluble, infusible products, to which the structure $R_2I^+Y^-$, where Y can be IF_4^-, IF_6^-, or IF_8^-, has been attributed on the basis of X-ray diffraction analysis. A method has been proposed for the synthesis of diarylbromonium salts having the general formula $(XC_6H_4)_2Br^+BF_4^-$ by treating arenes,[151] organomercury compounds,[152] or tetra-arylstannanes[153] with BrF_3 and boron trifluoride etherate in methylene chloride and acetonitrile at −70 °C.

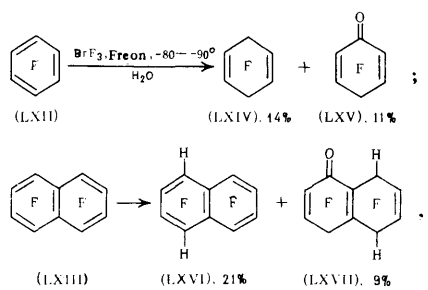
Interesting results have been obtained on treating aromatic polyfluoro-compounds with complexes of halogen fluorides.[154-157] Non-fluorinated arenes decompose and char on treatment with such complexes.[154]

Hexafluorobenzene and pentafluorobenzene do not react with IF_5 even at 120 °C. The reaction of trifluorobenzene and pentafluorobenzene with salts of the type $IF_4^+SbF_nCl_{6-n}$ in hydrogen fluoride, IF_5, or SO_2FCl at 15–50 °C with subsequent hydrolysis of the reaction mixture yielded aromatic derivatives of quinquevalent iodine—μ-oxotetrakis(polyfluoroaryl)dichlorodifluoroiodates:

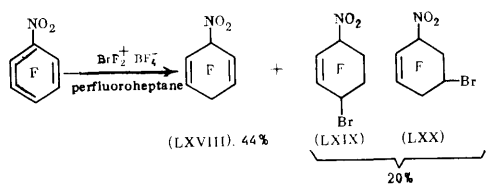


Ar_F = 2, 4, 6-$C_6H_2F_3$, C_6F_5 .

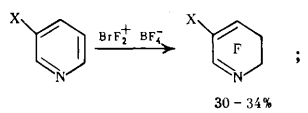
Bromine trifluoride reacts with pentafluorobenzene in Freon-114 or SO_2ClF with formation of bromopentafluorobenzene (27%); in an analogous reaction hexafluorobenzene (LXII) yields after hydrolysis perfluorocyclohexa-1,4-diene (LXIV) and hexafluorocyclohexa-2,5-dien-1-one (LXV); perfluoro-1,4-dihydronaphthalene (LXVI) and octafluoro-1-oxo-5,8-dihydronaphthalene (LXVII) are formed from octafluoronaphthalene (LXIII):[155]



Octafluorotoluene and 4*H*-heptafluorotoluene do not react with BrF_3 under these conditions, while pentafluoronitrobenzene and pentafluoropyridine do not react even at 20° to 30 °C. However, these compounds do react with difluorobromonium tetrafluoroborate $BrF_2^+BF_4^-$ at temperatures in the range between −80° and 0 °C. Pentafluoronitrobenzene is then converted into heptafluoro-1-nitrocyclohexa-1,4-diene (LXVIII) and a mixture of 4(5)-bromo-octafluoro-1-nitrocyclohex-2-enes (LXIX) and (LXX):



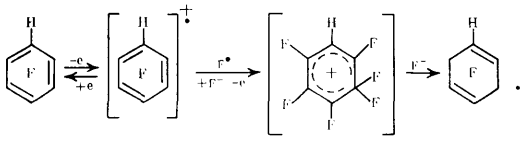
The fluorination of 3-halogenopyridines by this complex proceeds regiospecifically and leads to conjugated 3-substituted perfluoro-1-azacyclohexa-1,3-dienes:



X = Cl, F .

A similar study of the behaviour of aromatic polyfluoro-compounds in relation to BrF_3 and BrF_2^+ led Bardin et al.[155] to the conclusion that these reagents differ little in their electrophilicities, but the BrF_2^+ cation is a much stronger oxidant. Evidence is adduced in support of the view that the reactions of aromatic fluoro-compounds with bromine trifluoride and its complexes proceed via the one-electron

oxidation of the aromatic hydrocarbons with formation of radical-cations and their subsequent fluorination:[155–157]



It has been shown[158] that polyfluoroarenes are fluorinated via an analogous mechanism with xenon fluoride in hydrogen fluoride and by xenon fluoride complexes.

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It follows from the data examined that halogen fluorides are promising fluorinating agents which are suitable for the synthesis of practically important organofluorine products. The development of organic synthesis of the basis of these reagents is only just beginning.

From the preparative standpoint, we believe that chlorine monofluoride is of greatest interest. This applies particularly to the substitutional fluorination reactions of organic bromo- and chloro-derivatives. The waste products in the fluorination of such compounds with hydrogen fluoride are hydrogen halides, whose utilisation constitutes a difficult problem. In the fluorination reactions with the aid of ClF the side products are molecular halogens, which can be employed in the synthesis of the initial substrates.

In contrast to the majority of other fluorinating agents, chlorine monofluoride has the unique ability to introduce successively into an organic molecule one, two, and more fluorine atoms by substitutional fluorination. This constitutes yet another advantage of this interesting reagent.

The theoretical aspects of the reactions of halogen monofluorides and polyfluorides are also of undoubted interest. Chlorine monofluoride and the related compounds of the type HalY, where Y is a residue of a strong acid, not only add to multiple bonds but also abstract halogens from organic halogeno-derivatives under mild conditions via an electrophilic mechanism, which is usually not characteristic of the majority of other electrophiles (for example, HHal, RSHal, etc.). This group of reagents does not fit the classification of electrophiles which provides for their subdivision into two categories—strong and weak—depending on whether or not skeletal rearrangements take place following their addition to the $>C=C<$ bond.[159]

There is apparently no need for such a general classification of all electrophiles. The reactions of carbonium ions, occurring in the second stages of electrophilic processes, are associated solely with the characteristics of the structure of these intermediates and with their tendency to rearrange under particular conditions.

The unambiguous demonstration of a two-stage mechanism of the addition of ClF to the majority of unsaturated compounds in a non-polar medium[108] makes it impossible to agree with the conclusion that the initial molecules interact intermolecularly without the conversion of the intermediate molecular complexes into carbonium ions in non-polar media.[160] This conclusion was reached[160] on the basis of a theoretical study of the mechanism of the electrophilic addition reactions from the standpoint of the conservation of orbital symmetry.

It is to be expected that in the immediate future halogen fluorides will occupy their due place both in the industrial synthesis of organofluorine products and in theoretical organic chemistry.

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Translated from *Uspekhi Khimii*, 53, 2056-2077 (1984) U.D.C. 541.15 + 541.64 + 661.728

The Radiation Chemistry of Cellulose

B.G.Ershov and A.S.Klimentov

The radiation-chemical transformations of cellulose and the influence of various factors on the efficiency of these processes have been examined. Ionising radiation has a significant influence on the structural-morphological state of the polymer; the nature of the primary radical-ion radiolysis products has been discussed, and a quantitative description of the radiation degradation of cellulose has been given. The mechanism of the radiation-chemical transformations of cellulose, which provide a promising method for treating cellulose-containing raw material for the production of valuable products, has been discussed. The bibliography contains 131 references.

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I. INTRODUCTION

Cellulose is one of the most widely encountered natural polymers, being the principal component of plant materials. The study of the radiation chemistry of this compound is therefore of considerable theoretical and practical importance. The use of penetrating ionising radiation can radically alter the technology of the treatment of plant raw material, since it facilitates considerably the conversion of the carbohydrate complex into the soluble state or increases its sensitivity to other methods of treatment, such as enzyme hydrolysis.

The use of radiation with a high penetrating power (γ-rays, X-rays, accelerated electrons) makes it possible to bring about chemical transformations in the bulk of the substance, and this, in particular, has found extensive practical application as a method for modifying polymers.[1-5] Not all the reactions taking place when a substance is irradiated are specific for radiation chemistry. Many of them also apparently take place under the influence of light, an electric discharge, cavitation processes, etc. Thus the study of the radiation-chemical reactions is also important for establishing the mechanism of the chemical reactions taking place after initiation by other methods.

Considerable attention has been and is being paid to the problem of the influence of penetrating ionising radiation on cellulose and cellulose-containing materials. This is due to a number of factors, among which the following are of primary importance. The physical and chemical properties of cellulose fibres can be changed in a directed fashion by the radiation grafting of various polymers on to them.[6,7] Penetrating radiation achieves effective sterilisation of cellulose-containing materials for medical purposes, and the conservation of good and animal feedstuffs.[8-10] Irradiation is used to accelerate and optimise the processes involved in the thermochemical and enzyme treatment of wood,[11-17] cellulose,[18-20] and cellulose-containing waste products,[21-23] to modify the physicomechanical properties of wood and to create new materials based on it,[24-26] to intensify the production of yeast[27-31] and cellulose paper production.[32-35] Finally, ionising radiation may find application in the technology of the treatment of non-edible plant materials (chiefly the waste products from the wood processing industry and agriculture) to obtain animal feedstuffs and food products.[21,36-38]

A systematic analysis of data on the radiation chemistry of cellulose was last carried out in the 1970's.[39] The present review summarises the experimental data obtained in recent years, discusses the influence of radiation on the properties of cellulose, and examines the main trends in radiation-chemical transformations of this important natural polymer. Since the final products of the radiation-chemical transformations of cellulose have not been studied in detail, because of the fundamental difficulties involved in the chemical analysis of the long polymer fragments, the possible mechanisms of the transformations will be discussed using available data on the radiolysis of various simple carbohydrates and oligosaccharides, which can (in a certain sense) be regarded as model compounds of cellulose.

II. INFLUENCE OF IRRADIATION ON THE STRUCTURE OF CELLULOSE

Each monomeric unit in cellulose has three hydroxyl groups, which form intra- and intermolecular hydrogen bonds. The presence of the branched system of hydrogen bonds determines to a considerable extent the physicochemical and mechanical properties of the polymer.

Cellulose is one of the polymers whose crystallographic characteristics have been studied most intensively for several decades. Nevertheless, there is still lack of agreement about the phase compositions of cellulose. As early as the 1930's, Kargin[40] suggested that the amorphous state of cellulose is thermodynamically stable and the only state possible. Later, he drew attention to the main indications confirming this viewpoint.[41] At the present time, however, the more generally accepted approach regards cellulose as a material with a crystalline structure containing quantities of an amorphous phase. Different models of the crystallographic lattices of cellulose and theories of the crystallinity of this polymer exist. In particular, four structural forms of cellulose have been established, of which the natural material is described as cellulose I.

The structural state of cellulose has been described in detail.[42-44] It is suggested that cellulose consists of small crystallites, made up of microfibrils, which are surrounded by regions of amorphous and polycrystalline phases.[45,46]

The dimensions and orientation of the crystallites and the ratio of the phases are determined by the nature of the previous treatment of the materials. The length of the polymer chains is appreciably greater than the size of the crystallities, so that the macromolecules are present in alternating regions with crystalline and amorphous structures.

The complex amorphous–crystalline system can be characterised by the degree of crystallinity and the degree of orientation. The crystalline phase is more closely packed, so that the rates of hydrolytic splitting differ considerably for these phases. Different methods for determining the degree of crystallinity of cellulose generally give different results. This is because the methods used make it possible to study different aspects and manifestations of the structural state. For example, X-ray diffraction characterises the degree of order of the polymer, whereas methods involving chemical reaction determine the accessibility of the different regions to the reactions, that is they characterise its structure only qualitatively. Nevertheless, it is assumed[42–46] that cotton cellulose contains ~65–75% crystalline fraction and ~25–35% amorphous fraction.

The different manifestation of structurally sensitive properties in different regions of cellulose, however, is not sufficient to enable them to be characterised as amorphous or crystalline phases. It is apparently more correct to say that cellulose contains regions with different ratios of intra- and intermolecular ordering.[47] From this viewpoint, cellulose is regarded as a single-phase system, in which, if an amorphous phase is present, its concentration does not exceed ~5%.[48–50] According to this hypothesis, cellulose contains imperfect regions, and its structure can be regarded as "liquid-crystalline" or "paracrystalline".[48–50] The indeterminacy of the interpretation of the structural state of the original cellulose makes it difficult to explain the data obtained after it has been exposed to ionising radiation.

The structure and intensity of the infrared spectra of cellulose is preserved after its irrdiation up to an absorbed dose of ~100 kGrad,[51] from which is was concluded that its structure is preserved under these conditions. X-Ray diffraction has shown that the phase state of cellulose[52,53] and cotton lint[54] remains unchanged at much higher doses.

Infrared (IR) spectroscopy is most convenient for the study of the structure of cellulose if the phase changes are not accompanied by a significant change in the chemical state. On irradiation, however, the process with the greatest influence on the IR spectra is the chemical transformation of cellulose, that is the formation of carbonyl and carboxyl groups, dehydrogenation, and dehydration. In the study of the influence of radiation on the structure of cellulose, the strong band in the range 3600–3000 cm^{-1}, due to OH group stretches, is of particular interest. It can be used to characterise the redistribution of OH groups with respect to hydrogen bond strengths. With interest in the absorbed dose, the maximum of the band due to the OH groups in the infrared spectrum of cellulose is displaced from 3400 cm^{-1} to 3440 cm^{-1}, accompanied by a change in the shape of the band.[53] Table 1 gives the values of ν_{OH}, and also the symmetry index of the band a/b, that is the ratio of the right-hand and left-hand parts of the half-width of the band due to the OH groups. The observed changes show that irradiation leads to breakdown of the ordered system of intermolecular hydrogen bonds, as a result of which the hydroxyl groups are involved in less stable hydrogen bonds.[55] The distribution of OH groups with respect to bond strengths becomes statistically less uniform (the value of a/b changes from 0.72 to 0.58). The irradiation of cellulose leads to the production of carbonyl and carboxyl groups. The intensity of the corresponding bands in the infrared spectra (bands at 1740 cm^{-1} for CO and at 3400 cm^{-1} for COOH) increases with increase in the absorbed dose, and the change in their ratio (D_{1740}/D_{3400}) indicates the preferential formation of carbonyl groups (Table 1).

The changes in the structure of cellulose brought about by the action of γ-radiation have been characterised not only by IR spectroscopy but also by X-ray diffraction.[52,53] Up to absorbed doses of 480–1180 kGrad, the structure of cellulose remains practically unchanged[52] (since the values of the crystallinity indices, determined by the published method,[56] remain unchanged). At absorbed doses greater than 2000 kGrad, the crystallinity index decreases considerably (Table 2), and at a dose of 9400 kGrad, X-ray diffraction indicates that cellulose can be characterised as having an amorphous structure.

Table 1. Changes in the infrared spectra of cotton cellulose γ-irradiated in a vacuum.[53]

Dose, kGrad	ν, cm^{-1}	a/b	D_{1740}/D_{3400}
0	3400	0.72	0
480	3410	0.67	0.4
2560	3420	0.65	1.1
9400	3440	0.58	3.7

Table 2. Physicochemical properties of γ-irradiated cotton cellulose.[53]

Dose, kGrad	β, %	$\overline{DP}_\nu$	c_s, %	$\overline{DP}'_\nu$	β′, %
0	73	911	10.3	205	78
5	73	575	10.9	189	78
10	73	505	11.3	159	78
32	73	269	11.9	139	78
170	73	94	17.0	80	78
480	73	49	21.2	48	76
680	—	40	22.0	28	73
800	—	32	27.8	10	72
1680	69	14	43.7	5	68
2560	63	8–9	100	—	—
9400	0	4–5	100	—	—

Notes: β is the crystallinity index of the original cellulose, $\overline{DP}_\nu$ its viscosity-average degree of polymerisation, c_s the quantity of soluble fraction in the ethanolysis of the cellulose (% of the mass of the original specimen), $\overline{DP}'_\nu$ the viscosity-average degree of polymerisation of the insoluble residue, and β′ its crystallinity index.

γ-Irradiation leads to the degradation of cellulose, revealed by a decrease in its degree of polymerisation. The changes in the degree of polymerisation of cellulose and in its solubility take place much more effectively (see Table 2) than the changes in the structure observed on the X-ray diffraction patterns. This apparently represents a situation where the method for the experimental determination of the degree of ordering of a substance in practice makes it possible to estimate only a certain particular characteristic. Thus X-ray diffraction indicates the existence of a highly ordered structure in cellulose up to high absorbed doses. At the same time, chemical methods for the analysis of the structure of cellulose, which to a large extent characterise the accessibility of the different parts of its molecule with respect to the reactions and breakdown of the system of intermolecular hydrogen bonds, indicate that γ-irradiation leads to the production of disordered defect regions. There is no contradiction here, however. X-Ray diffraction shows that

in the dose range studied, the structure of the primary crystals and the overall degree of crystallinity of cellulose remain unchanged. The increase in the ability of γ-irradiated cellulose to dissolve, however, is related to an appreciable decrease in its degree of polymerisation, and also to the formation of active chemical groups, i.e. carbonyl and carboxyl groups, which facilitate the conversion of the macromolecules to the dissolved state. Thus when irradiated cellulose is brought into contact with water, the products transferred preferentially to the solution are those containing acidic and aldehydic groups, and the total extractability increases with increase in the absorbed dose.[57]

The change in the degree of order of the cellulose structure on irradiation has been characterised by IR spectroscopy.[58] The parameter of the degree of ordering (φ) (the term "index of paracrystalline regularity" is used in the work cited) was the ratio of the intensities of the bands at 1370 cm^{-1} and 890 cm^{-1}. The parameter φ decreases almost exponentially with increase in the absorbed dose, and for a dose of ~2400 kGrad it decreases by a factor of e. Infrared spectroscopy apparently determines the degree of ordering of the largest macromolecules of cellulose, and it shows a closer correlation, compared with X-ray diffraction, with chemical methods for estimating its structural state. The observed character of the decrease in the degree of ordering of the cellulose structure with increase in the absorbed dose agrees with the decrease in its degree of crystallinity determined in Ref.59.

In the γ-irradiation of cotton fibres, even at an absorbed dose of ~10 kGrad, scanning electron microscopy detects unambiguously the breakdown of their morphologicaly structure.[58] Cracks lying parallel to the twisting axis of the fibre appear, and show a significant increase in their length and depth with increase in the absorbed dose. This process is apparently due to the rupture of intermolecular bonds in the fibrils and to a decrease in the strength of the surface interactions between them. Various problems of the morphology on irradiated cellulose materials were examined in Ref.34. The physicochemical processes taking place when cotton fibres are exposed to radiation lead to an appreciable decrease in their mechanical strength.[58,59]

Thus the action of ionising radiation leads to a decrease in the intra- and intermolecular ordering in cellulose, due to the breakdown of the system of intermolecular hydrogen bonds and to chemical transformations of the polymer.

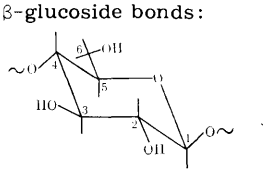
III. RADICAL RADIOLYSIS PRODUCTS OF CELLULOSE

The radicals produced by the radiolysis of cellulose have been studied many times by EPR.[39,60,70] In spite of this, there was lack of agreement on their nature until recently. This was due to the fact that the studies were carried out under different conditions (temperature of irradiation, moisture content of the cellulose, absorbed doses etc.), and in the interpretation of the EPR spectra, no allowance was made for the actual conformation of the monomeric fragment of the polymer. As a result, the EPR spectrum of γ-irradiated cellulose was examined in different studies as, for example, consisting of a triplet and a quintet[39] or a quadruplet and a singlet.[69]

The radicals in γ-irradiated cellulose, and the kinetics of their accumulation and thermal transformations, have been studied.[71,74] Natural cotton cellulose, purified and dried for a long time at 313 K (in the presence of P_2O_5) and at 378 K, and also moist cellulose, containing two water weight fractions, were used. Cellulose hydrate (technical cellophane) and holocellulose were also studied. The most interesting data were obtained on the radicals obtained by irradiating cellulose at a low temperature (77 K). It may be assumed that under these conditions the species stabilised are the primary radical–ion products, whose subsequent chemical transformations determine the entire range of changes in the physicochemical state of cellulose. Specimens of natural and regenerated cellulose irradiated at 77 K acquire a bluish colour,[71,72] typically observed when electrons are captured by intermolecular traps in polar substances.[73–75] The colour disappears rapidly under the influence of visible light or when the specimen is heated to ~173 K. The changes which then take place in the EPR spectrum indicate the disappearance of the narrow singlet, due to the captured electron, with a g value equal to that for the free electron. The optical absorption maximum for the captured electron (e_{capt}) in cellulose hydrate lies at 540 ± 20 nm, and the half-width of the absorption band is 1.3 1 0.1 eV, which are close to the characteristics of the optical spectra of e_{capt} in vitreous polyhydric alcohols[75–78] and concentrated aqueous solutions of carbohydrates.[79,80] In this case, the stabilisation apparently takes place in the water micro-phase in cellulose with a vitreous structure, and also in the amorphous regions of cellulose in the electrostatic field of the oriented OH groups. The yield of this species is much lower than that of the other radicals.

The EPR spectra of natural cellulose and cellulose hydrate are practically identical, and (in addition to the e_{capt} signal) consist of the superposition of a triplet (component ratio close to 1 : 2 : 1), splitting between the components 2.6 ± 0.1 mT), a doublet (splitting 3.0 ± 0.2 mT), and a singlet with a low intensity.

The cellulose macromolecule includes D-glucose repeat units, joined by 1,4-β-glucoside bonds:



The three-dimensional structure of the D-glucose unit in the macromolecule is characterised by a pyranose ring with axially arranged hydrogen atoms. An analysis of the splitting constants indicates that the signals with the doublet and triplet HFS are due to radicals with a pyranose ring, formed as a result of the rupture of the C–H bonds in positions 1, 2, 3, or 4. This follows from the fact that the spectrum does not show the signals with splitting constants 1.7–1.9 mT, characteristic of radicals with α-protons.[81–83] Splitting values of 2.5–3.0 mT are characteristic of carbohydrate radicals with axial β-protons.[84–87] As a result of the removal of the hydrogen, the hybridisation of the carbon atom changes from sp^3 to sp^2, and the unpaired electron is transferred to the $2p_z$ orbital; in this position, it interacts effectively with the axial β-hydrogen atoms. The doublet signal must be due to the radical formed by the rupture of the C–H bond in position 1. In principle, the triplet signal may be due to any of the radicals produced as a result of the rupture of a C–H bond in positions 2, 3, or 4; it may also represent the superposition of EPR signals from three radicals produced in this way, differing little from one another. The most probable position for the localisation of the excitation energy, however, is the C(4) atom. This conclusion agrees with the fact that the C–H bonds broken are those in positions 1 and 4, which are weakened to the greatest extent as a result of the withdrawal of the electrons to the 1,4-β-glucoside bonds and the ring oxygen atom. A similar interpretation was proposed for the EPR spectra obtained in the sensitised photolysis[88] and radiolysis[89] of cellulose.

The appearance of the singlet signal can apparently be related to the presence of residual lignin in the cellulose. Thus the intensity of this signal is much greater in the EPR spectra of holocellulose and wood γ-irradiated at 77 K.[71] Unlike cellulose, these materials contain considerable quantities of lignin (particularly wood). Lignin γ-irradiated at 77 K gives a narrow symmetrical singlet with line width 1.0 ± 0.1 mT, which coincides with that observed for cellulose and wood.[72] This may indicate that the singlet signal in the spectrum of irradiated cellulose is due to a radical of the "lignin" type. The yields of the radicals, calculated for a linear accumulation section (G), are 3.4 radicals and 1.6 radicals per 100 eV for the γ-irradiation of specimens at 77 K and 300 K respectively.[71] The kinetics of the accumulation of the radicals is described effectively by the equation:

$$[R] = [R]_{lim}(1 - e^{-K_d D})$$

where the limiting concentration of the radicals $[R]_{lim} = G/K_d$ (K_d is the constant for the radiation disappearance of the radicals), and the absorbed dose $D = It$ (I is the dose power, and t the irradiation time). The values $K_d = 7.7 \times 10^{-3}$ kGrad^{-1}, calculated from this equation using published data,[71] are the same, within experimental error, for γ-irradiation at 77 K and 300 K, apparently indicating that the mechanisms of the annihilation of the radicals by radiation at these temperatures are the same. This value of K_d is characteristic of compounds with saturated bonds,[90] and indicates that there is no effective migration of the excitation in cellulose.

Thus when cellulose is exposed to ionising radiation, some of the "ejected" electrons, after thermalisation, are stabilised in intermolecular traps. Because of the "crystal-like" character of the structure of cellulose, however, the concentration of these traps is apparently insufficient to suppress effectively the recombination of the "electron-hole" ion pairs, bound to Coulombic interaction. The excitations produced as a result of the recombination are localised, leading to the rupture of the C–H bonds in the weakened positions 1 and 4 [$R_{C(1)}$ and $R_{C(4)}$ radicals respectively are formed]:

$$(RH)^* \rightarrow \dot{R} + H\ .$$

The hydrogen atoms dehydrogenate the elementary monomeric units of cellulose, again in positions 1 and 4. Another important fact is noteworthy. In very moist cellulose, γ-irradiated at 77 K, OH radicals are stabilised, and with increase in temperature these disappear, removing preferentially the hydrogen atoms in positions 1 and 4 of the carbohydrate fragment.[71,72] Thus the point of attack by the radical coincides with the point of rupture of the C–H bonds in the direct action of radiation on cellulose:

$$RH + H(OH) \rightarrow R_{C(1)}\,(R_{C(4)}) + H_2(H_2O).$$

The large amount of information on the EPR study of cellulose γ-irradiated at room temperature is fairly contradictory. Thus it has been reported[65] that the spectrum consists of the superposition of a singlet and a triplet. In Refs. 63, 64, and 67 it is reported that the EPR spectra of dried cellulose I and II after γ-irradiation are extremely similar, and consist of poorly resolved triplets. The EPR spectra produced when the dry specimens are brought into contact with water, and the spectra of specimens containing residual moisture, consist of three components for cellulose I, and five lines for cellulose II. An EPR spectrum containing five components was recorded in Ref.60. Under certain conditions, preliminary treatment of cellulose in the absence of oxygen gives signals with a doublet structure.[67,68]

The present authors[71,72] established that the EPR spectra of very moist cotton cellulose and cellulose hydrate, γ-irradiated at 77 K and then heated to 300 K, and also specimens γ-irradiated directly at 300 K, are practically identical and consist of a triplet with splitting between the components ~2.8 mT. When the specimens are subsequently heated, the total concentration of radicals decreases, the structure of the EPR spectrum changes, and there are grounds for assuming that it consists of the superposition of the EPR signals from several radicals (singlet, doublet, and triplet). At 330 K, a doublet signal with a splitting less than 1.5 mT predominates in the EPR spectrum.

These differences in the structures of the EPR spectra observed in cellulose γ-irradiated at room temperature are apparently due to the appreciable influence of the structure of the cellulose, its moisture content, and other factors, which are not taken into account in the preparation of the cellulose specimens and which influence the thermal stability of the radicals. As a result, at a given temperature (room temperature), radicals of several types, but with different concentration ratios, are stabilised in different specimens, leading to appreciable differences in the form of the EPR spectra.

Thus a study of the thermal stability of cellulose macroradicals[39,61–64,69,89] showed an appreciable increase in the rate of their disappearance or transformation in the presence of water, aqueous solutions of acids and alkalis, ammonia, etc. In thoroughly dried cellulose, the temperature of the intensive disappearance, corresponding to a decrease in the original concentration of radicals by a factor of two, corresponds to ~370 K, whereas in the presence of 2, 7, 11, and 24 mass % water it is displaced to 310, 260, and 210 K respectively.[89] This effect is attributed to the plasticising action of water on cellulose, leading to an increase in the molecular mobility in the polymer. The disappearance of the radicals is then limited by the mobility of the macrochains in the cellulose, and the actual nature of the radicals apparently has no significant influence on the rate of their disappearance. The thermal stability of ~15% of the macroradicals is independent of the water concentration, apparently because they are localised in crystalline regions which are not accessible to water.[89]

The disappearance of the macroradicals is characterised by a kinetic arrest; thus when a certain temperature is reached, the concentration of the particles, for a limited observation time, can be regarded as "stationary". Thus the disappearance of the radicals takes place as it were "in stages". The polychromatic kinetics are due to the physical non-uniformity of the polymer matrix, as a result of which a number of chemically identical processes with different values of the rate constants of the limiting stages take place, that is there is a distribution of the rate constants with respect to activation energies (from E_{min} to E_{max}). Analysis of the results established[89] that for dried cellulose, the pre-exponential factor in the Arrhenius equation is ~10^{-5} cm^3 s^{-1}, E_{min} = 96 ± 8 kJ mole^{-1}, and E_{max} = 155 ± 12 kJ mole^{-1}. For specimens containing ~50% water, the pre-exponential factor decreases to ~10^{-13} cm^3 s^{-1}, and E_{min} and E_{max} have the values 29 ± 2 kJ mole^{-1} and 46 ± 2 kJ mole^{-1} respectively.[89] A noteworthy feature is that in cellulose there may be a compensation effect, involving a decrease in the activation energy of the process with increase in temperature.[91] This feature leads to a decrease in the observed values of the activation energies for the disappearance of the radicals.

When cellulose is plasticised by water, the diffusion mobility of the macro-radicals increases by several orders of magnitude. The elementary act of their diffusion apparently involves the movement of the pyranose unit, in which the

radical state is localised, relative to the other units of the polymer. In dry cellulose, each unit is joined to its neighbours by three hydrogen bonds, but when water is introduced, these bonds are broken, leading to a decrease in the strength of the bonding to the polymer macromolecules. This is responsible for the plasticising action of water or other low-molecular substances on cellulose.

The results of the experimental study of the EPR spectrum show that no appreciable rupture of C–OH, C–C, or C–O–C bonds takes place when cellulose is γ-irradiated. The secondary reactions of the radicals obtained by the rupture of the C–H bonds in positions 1 and 4 lead to the rupture or breakdown of the molecular structure of cellulose.

IV. RADIATION-CHEMICAL DEGRADATION OF CELLULOSE

When polymers are irradiated, two opposed processes take place: cross-linking of the polymer chains, leading to an increase in the average molecular mass $\overline{M}$, and also their degradation, leading to a decrease in the value of $\overline{M}$.[1–5] These processes most frequently take place simultaneously, and polymers may undergo cross-linking or degradation, depending on which process predominates. Cellulose undoubtedly belongs to the second group; degradation is the main result of the action of ionising radiation on cellulose.[7,11,17,19,51,53,92–103]

1. Degradation of the Polymer According to a Random Law

Since the radiation-chemical processes involved in the rupture and cross-linking of polymer chains take place according to a random law, the changes in the molecular mass distributions of the macromolecules are described using statistical methods. The regular statistical features of the processes of cross-linking and degradation, taking place under the influence of ionising radiation, have been discussed in detail.[1,3,5] If the original polymer has a distribution with respect to degrees of polymerisation close to the most probable distribution, the degree of polymerisation will decrease during disordered degradation, but at the same time the most probable distribution will be preserved. For this case, the following equation is applicable:

$$\overline{DP}_n/\overline{DP}_n^0 = \overline{DP}_w/\overline{DP}_w^0 = 1/(1+s) \qquad (1)$$

where $\overline{DP}_n$ and $\overline{DP}_w$ are the number-average and weight-average degrees of polymerisation, $\overline{DP}_n^0$ and $\overline{DP}_w^0$ the corresponding original degrees of polymerisation, and s the number of ruptures taking place in the original polymer molecule. For the most probable distribution, $\overline{DP}_w = 2\overline{DP}_n$.

A system with a broader original distribution of the polymer with respect to degrees of polymerisation, compared with the most probable distribution, shows a slight deviation from relationship (1). It should be emphasised, however, that the most probable distribution in real situations is reached in the initial range of absorbed doses, used for the analysis of the dependence of the degree of polymerisation on the number of ruptures, that is on the absorbed dose, according to Eqn. (1). The number of bond ruptures s for a molecule with a degree of polymerisation $\overline{DP}_n$ is given by the equation

$$s = \frac{D\,\overline{DP}_n^0 m}{N_A E_d} \qquad (2)$$

where m is the molecular mass of the unit fragment of the polymer, and E_d is the energy required for the rupture of one bond. Eqn.(1) can be transformed as follows:

$$\frac{1}{\overline{DP}_n} - \frac{1}{\overline{DP}_n^0} = \frac{G^0 m D}{N_A} \qquad (3)$$

Here, G^0 is the initial radiation-chemical yield of the process of polymer degradation, that is the number of macromolecule ruptures corresponding to 100 eV of absorbed energy.

The molecular masses of polymers (M) or their degrees of polymerisation are determined by measuring the viscosity of their dilute solutions. For an unbranched polymer (in particular cellulose[104,105]), the following empirical relationship is applicable:

$$[\eta] = KM_v^\alpha \qquad (4)$$

where K and α are the parameters which depend on the chemical structure of the polymer, temperature, and the solvent used, and $[\eta]$ the characteristic viscosity. Depending on the configuration of the polymer macromolecule in the solution and the nature of the bonds formed with the solvent, the values of α vary in the range 0.6–1.0, corresponding to changes of only 1.82–2.0 in the expression in braces in Eqn.(5).[3] The value of M_v is related to the number-average molecular weight M_n by the expression

$$M_v = M_n\{(\alpha+1)\Gamma(\alpha+1)\}^{1/\alpha} \qquad (5)$$

where $\Gamma(\alpha+1)$ is the γ-function of α.

Thus the experimentally determined value of M_v and Eqns. (3) and (5) can be used to determine the yield of the degradation of the polymer G.

2. The Radiation Degradation of Cellulose

The first systematic study of the degradation of cellulose under the influence of a beam of accelerated electrons with an energy of 0.8 meV (for sulphite cellulose and cotton linter) was described in Ref.11. The degree of polymerisation was determined from the characteristic viscosity of the irradiated specimens in solutions of the complex of copper(II) with ethylenediamine. A regular decrease in the viscosity, which was practically the same for the specimens indicated, was established, that is the degree of polymerisation decreased with increase in the absorbed dose.

Since the determination of $\overline{DP}_v$ in Ref.11 was inaccurate, because of the absence of a reliable relationship between η and M in Eqn.(4), another method of calculation was proposed,[92] which did not use any direct relationship between η and M. This gave the following final expression relating η and the absorbed dose d:[92]

$$\eta = A(D+D_0)^\alpha \qquad (6)$$

where D_0 is the absorbed dose corresponding to the attainment of the most probable distribution of the polymer with respect to molecular masses, α the coefficient in Eqn.(4), and A a constant determined from the experimental dependence of η on $D + D_0$ in accordance with Eqn.(6). Treatment of the data from Ref.11 showed[92] that $\alpha = 0.71$ and $A = 4.9$. The value of K in Eqn.(4) was then taken as 5.9×10^{-4}, which gave a value of 10 for the cellulose degradation yield†.

The approach proposed in Ref.92 has the same disadvantages [the approximate determination of the parameter D_0 (7.5 kGrad and 10 kGrad for sulphite cellulose and cotton linter respectively) in Eqn.(6), and the arbitrary choice of the value of K in Eqn.(4)]; moreover, the treatment in Ref.92 was based on the fundamentally unjustified assumption that the yield of the cellulose degradation process remains constant and independent of the absorbed dose. In Ref.92 it was pointed out that the determination of the degradation

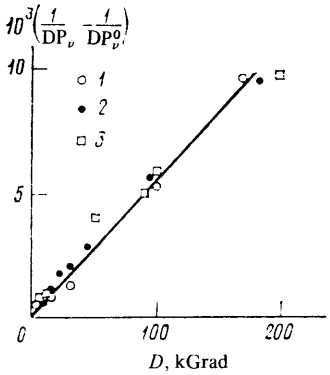
† According to Ref.58, the calculation of the yield in Ref.92 is erroneous, and the corrected value is only half the published value, that is 5.

yield has a low accuracy, because of a number of listed approximations in the calculation procedure.[3]

Later work[58] also used the approach proposed in Ref.92 and established that for cotton cellulose, $A = 4.0$, $\alpha = 0.78$, and $D_0 = 5$ kGrad. Taking from Ref.104 the value 1.71×10^{-4},[104] the value obtained[58] for the cellulose degradation yield was 4.5 ± 0.3.

There is apparently more justification for estimating the cellulose degradation yield using Eqns.(3) and (5), which are obtained from a statistical examination of the processes taking place. The degree of polymerisation in this case is determined from Eqn.(3), which relates it to the viscosity characteristics of the polymer solution. A solution of cellulose in Cd-oxene (a solution of the ethylenediamine complex of cadmium) is the most suitable for the measurement of the viscosity characteristics; this method has been widely used in recent years. According to Ref.105, the values of α and K in Eqn.(4) for this system are 0.94 and 7.1×10^{-3} respectively.

The dependence of $\overline{DP}_v$ for cellulose on the absorbed dose, constructed on the coordinates of Eqn.(3) (using data from Refs.53, 102, and 106), is shown in the Figure. It can be seen that Eqn.(3) is satisfied up to an absorbed dose of ~200 kGrad. In Ref.102, the characteristic viscosity was measured in a solution of the ethylenediamine complex of copper; the values of K and α were taken as 1.33×10^{-4} and 0.905 respectively.[107] In Refs.53 and 106, the characteristic viscosity was measured in Cd-oxene solutions. Since for the values of α used in the works cited[53,102,106] the number-average and viscosity-average degrees of polymerisation are related by the expression $\overline{DP}_v = (1.90\text{–}1.96)\overline{DP}_n$,[3] the radiation cellulose degradation yield, determined from the data given in the Figure, is 7.2 ± 0.2. The applicability of Eqn. (3) indicates that the radiation degradation of cellulose does in fact take place according to a random law.



Plot of $1/\overline{DP}_v - 1/\overline{DP}_v^0$ against the absorbed dose (*1*—Ref.53, *2*—Ref.102, *3*—Ref.106).

Eqns.(1) and (3) are applicable for the most probable distribution of the molecular weights of the polymer. For real specimens, which have a broad original degree of polymerisation distribution, some deviation from the linear relationship between $(\overline{DP}_v)^{-1}$ and the absorbed dose can be expected in the initial stages of the irradiation, as far as a certain dose D_0 corresponding to the attainment of the most probable distribution. It can be seen from the Figure, however, that if this deviation does take place for the data being considered at doses up to ~30 kGrad, it is very slight. At absorbed doses ≳ 200 kGrad, deviations from Eqn.(3) are observed, and the experimental data up to fairly large doses (~1000 kGrad) can be described effectively by the following empirical relationship

$$1/\overline{DP}_n - 1/\overline{DP}_n^0 = KD^m \ . \qquad (7)$$

According to Refs.53 and 102, the value of m in Eqn.(7) is 0.83; Ref.98 gives the value 0.73 (the dose D is expressed in kGrad).

The deviation of the experimental data at high absorbed doses from the relationship (3) predicted on the basis of simple statistical considerations is apparently due to the fact that irradiation is accompanied not simply by depolymerisation of the cellulose, and the rupture of the bonds in the macromolecules is accompanied by the formation and accumulation of radicals which are stable at room temperature, and also new functional groups. The latter are apparently formed at the points where the cellulose polymer chains are ruptured. The presence of these polar groups influences, firstly, the values of the effective characteristic viscosity of the solutions of the irradiated cellulose, used to determine the average molecular mass. Secondly, the C=O groups, like the free radicals, act as effective acceptors of electrons and excited states, formed during the irradiation of various substances. Thus their accumulation during radiolysis leads to a decrease in the rate of the subsequent degradation of the cellulose. This is indicated by the results of a study[57] which established a significant decrease in the rate of the degradation of cellulose specimens containing carboxyl groups (monocarboxycellulose).

The radiation degradation of cellulose is accompanied by a decrease in the width of the molecular mass distribution, and with increase in the absorbed dose, a monodisperse distribution is approached. A decrease in the polydisperse character of technical celluloses at high absorbed doses (500–1000 kGrad) has been noted.[70,108] It has also been established[109] that a change in the molecular mass distribution of cellulose takes place even at low doses. Thus the non-uniformity coefficient decreases from 1.3 for the original cellulose to ~0.4 for irradiated cellulose (for an absorbed dose of 3.2 kGrad). A similar picture is observed for the radiolysis of native dextran, consisting of D-glucose units, joined by a 1,6-glucoside bond.[110] The ratio of the average molecular masses $M_z : M_w : M_n$ is 3.5 : 2.0 : 2.0, whereas for the degradation of the macromolecules according to a randam law, this ratio should have been 3 : 2 : 1.[1,3] This difference is apparently due to the characteristic features of the molecular mass distribution on fractionation, where no account is taken of the final values of the molecular masses and their distribution in the separate factors.

V. CHEMICAL TRANSFORMATIONS IN IRRADIATED CELLULOSE

1. Gas Liberation During the Irradiation of Cellulose

The action of ionising radiation leads to extensive chemical transformations in cellulose. When cellulose is irradiated, gaseous products are liberated: hydrogen, carbon monoxide, carbon dioxide[39,51,111] and small quantities of methane.[111] In the initial stages of irradiation (up to ~200 kGrad), the accumulation of the products is proportional to the absorbed dose (in a vacuum). The radiation-chemical yields of H_2, CO, and CO_2 for an absorbed dose of ~500 kGrad are respectively 1.3, 0.8, and 1.6 in a vacuum, and 1.2, 1.7, and 3.3 in an oxygen atmosphere.[39,51] A similar percentage ratio of the yields of the gases in the dose range 50–2500 kGrad is given in Ref.111.

2. Redox Transformations of Cellulose

An important role in the radiation-chemical transformation of cellulose is played by processes of redox degradation. The copper number (c.n.), which characterises the reducing power, increases considerably with increase in the absorbed dose.[102,106] Analysis has shown that carbonyl and carboxyl groups are formed in irradiated cellulose[39,51,102] (Table 3).

Table 3. Chemical analysis of cellulose γ-irradiated at room temperature.[102]

Dose, kGrad	$10^{-19}N_1, g^{-1}$	$10^{-19}N_2, g^{-1}$	P.p.m.
0	0.32	1.90	1.3
8.8	0.71	1.97	1.9
20.6	0.90	2.01	2.8
45.2	0.94	2.11	3.8
94.6	1.48	2.23	6.2
183.0	2.20	2.36	11.2
406.0	2.99	2.59	24.6
908.0	4.11	2.78	46.5
1880.0	4.84	3.04	70.2

Notes. N_1 and N_2 are the numbers of carbonyl and carboxyl groups respectively in one gram of cellulose.

The radiation-chemical yield of carbonyl and carboxyl groups is slightly lower for irradiation in a vacuum or in a nitrogen atmosphere than for irradiation in an oxygen atmosphere.[39,51,98] The yields of carbonyl groups are higher than the yields of carboxyl groups.[102] Thus for a specimen of dry cellulose γ-irradiated at room temperature in a closed volume for an absorbed dose of 8.8 kGrad, the yields of carbonyl and carboxyl groups were 7.6 and 1.3 respectively.[102] For irradiation by accelerated electrons (dose 3.7 kGrad), the yields of these groups are 7.8 and 3.1.[102] Other workers[39,51,93] give appreciably higher values for the yields: 58 (for the CO groups) and 3.5 (for the COOH groups). A yield of 3.6 for the carboxyl groups was also obtained in Ref.19.

It can apparently be assumed with sufficient accuracy that the yield of carboxyl groups in the radiolysis of cellulose is 3 ± 1. The values of the yields of the carbonyl groups given in Refs.102, 39, 51, and 93 differ considerably, but the most reliable value is apparently ~7–8.[102] The unusually high value obtained in Refs.39, 51, and 93 is probably due to the conditions of the analysis (this involved the hydrolysis of the oligosaccharides extracted by aqueous solution from the irradiated cellulose). An equally high yield (~50) can be obtained from the data given in Table 3 if it is assumed that the copper number provides a quantitative characteristic of the concentration of carbonyl groups in irradiated cellulose. Their accumulation at high absorbed doses takes place according to the same law as the degradation of the macromolecules [Eqn.(3)]. The data in Ref.102 gave the following relationship

$$c = BD^m$$

where c is the concentration of carbonyl or carboxyl groups, and B is a coefficient equal to 6.8×10^{-7} mole g^{-1} or 1.8×10^{-7} mole g^{-1} for the carbonyl and carboxyl groups respectively. The value of n for the radiation accumulation of carbonyl and carboxyl groups was the same and equal to ~0.5. In Ref.98, in an interpretation of published data[93] on the accumulation of COOH groups, the exponent m was found to be 0.69.

Because of the high molecular weight of cellulose and other polysaccharides, the use of the methods of chemical analysis, in particular chromatography and mass spectrometry, to determine the final radiolysis products is practically impossible. It was previously noted[97,112,113] that irradiated cellulose contains water-soluble and water-insoluble fractions. From the water-soluble fraction it was possible to isolate components soluble in ethanol, among which cellobiose, glucose, 2-ketogluconic acid, arabinose, glyoxal, and a number of other complex acids were detected.[97] The hydrolysis of the water-soluble fraction of radiolysed cellulose gives xyloses, arabinoses, glucuronic acid, formic acid, and malonic dialdehyde.[21] The following values were obtained for the radiation-chemical yields for the formation of some of these compounds: 48.7 ± 2.4 for glucose, 10.1 ± 2 for xylose, 0.016 for malonic dialdehyde, and 2.3 ± 0.2 for formic acid. The formation of pentosans has been reported.[102]

3. The Radiation-chemical Transformations of Various Model Carbohydrates

To establish the principal routes in the radiation-chemical transformations of cellulose and other polysaccharides, it is appropriate to use simpler carbohydrates, whose transformations, on the one hand, can model the chemical reactions taking place in polysaccharides, and on the other hand, can be studied by modern methods of chemical analysis.

These carbohydrates include cellobiose, which contains two glucose residues connected by a glucoside bond. This disaccharide can be regarded as a fragment of cellulose. In aqueous media, the greater part of the final radiolysis products of this carbohydrate (~98%) consists of glucose, gluconic acid, 5-ketoglucose, 4-deoxyglucose, 2- and 5-deoxygluconic acid, deoxyketoglucose, arabinose, dihydroxyacetone, ribose, erythrose, and various other compounds.[114,115] The mechanism of their formation involves the hydrolysis of radicals obtained by the rupture of the C–H bonds in positions 1 and 4 and partly 5.

The cellobiose decomposition yields depend on the nature of the gas saturating the aqueous solution. Thus in a nitrogen atmosphere, the radiation yield is 3.1, and increases to 6.5 when the solution is saturated with nitrous oxide.[116] Since in the last case the hydrated electrons formed are converted into OH radicals:

$$N_2O + e(aq) + H_2O \rightarrow N_2 + OH^- + OH\ .$$

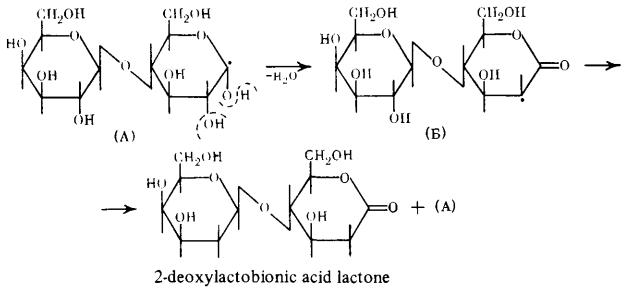
The observed doubling of the disaccharide decomposition yield most probably indicates that OH radicals play a decisive role in their radiation-chemical transformation. The role of the OH radicals most probably reduces to the removal of an H atom from the C(1) or C(4) atoms with the subsequent hydrolytic splitting of the radical at the glucoside bond.

According to Ref.117, the yield for the breakdown of the glucoside bond in cellobiose decreases by a factor of about 2.5 in the presence of oxygen. This is apparently due to the addition of an O_2 molecule to the C(1) or C(4) atoms with the formation of a peroxide radical and other transformation paths different from the rupture of the glucoside bond. Thus the radiolysis of aqueous solutions of cellobiose, as in the case of many other disaccharides (see the published monograph[118]), involves the rupture of glucoside bonds, oxidation, redox degradation, and the formation of deoxy- and deoxyketo-compounds.

A number of carbohydrates show appreciable radiation-chemical instability in the polycrystalline state. In this case the radiolysis is accompanied by the formation of a limited number of products. For example, the radiation-chemical

transformations of α-lactose monohydrate take place with a yield of 40–60 [119] according to three main schemes.[120]

Scheme 1

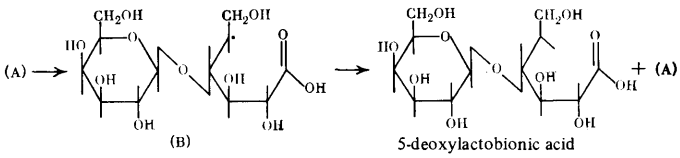


2-deoxylactobionic acid lactone

The radical (A) formed on γ-irradiation loses water as a result of dehydration; this gives the radical (B), which removes an H atom from the C(1) atom of a neighbouring lactose molecule. This gives 2-deoxylactobionic acid lactone, and also a new radical (A). Thus a chain process is initiated, in which the yield of lactone is 20.

The reaction involving the radical (A) can also take place by another mechanism to give the radical (C). The radical (C) removes an H atom from a neighbouring molecule, and as a result of a chain mechanism gives the final product 5-deoxylactobionic acid with a yield $G = 40$.[120]

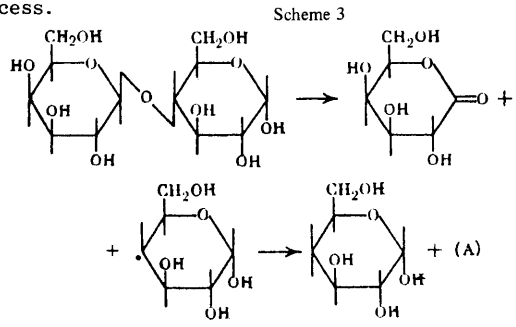
Scheme 2



5-deoxylactobionic acid

The rupture of the glucoside bond apparently takes place according to scheme 3 with the participation of a radical in which the electron is localised on the C(4) atom to give galactonic acid lactone ($G = 4.5$) and 4-deoxy-*D*-glucose ($G = 4.5$).[120] This process is not a chain reaction, unlike the two previous ones. The radical (A) is also generated in this process.

Scheme 3



Similar reactions take place in other systems. For example, the radiation-chemical transformations of 2-deoxy-*D*-ribose give 2,5-dideoxyerythropentonic acid with yield $G \geq 650$.[121] Crystalline *D*-fructose also decomposes under the influence of radiation, with a yield of 40–60.[122]

These examples show that for a number of carbohydrates, radiation-chemical decomposition takes place by a chain process. It is important to emphasise, however, that the yield of products associated with the rupture of the glucoside bond is low, and corresponds to the usual yields of the decomposition of substances by a non-chain mechanism. Thus 4-deoxy-*D*-glucose and galactonic acid lactone are formed by the rupture of the glucoside bond of α-lactose monohydrate by a non-chain mechanism with a yield of 4.5. This is an extremely important feature, since the yield for the degradation of cellulose (~7) indicates that a non-chain mechanism is most probable for the rupture of the glucoside bonds. Because of the contradictory nature, noted above, of the data relating to the yield of carbonyl groups (~7.6 [102] and ~58 [39,51,94]), however, a chain process in the radiation-chemical decomposition of cellulose by reactions analogous to those just examined cannot be finally excluded.

It has also been suggested that cyclic oligosaccharides—cycloamyloses—be used as model compounds imitating the radiation-chemical transformations of cellulose and other biological polysaccharides.[123,124] These compounds also do not have free reducing groups, that is aldehyde and keto-groups, whose presence in simple carbohydrates is responsible for the chemical properties which they exhibit.

It has been reported[125] that the γ-irradiation of cyclohepta-amyloses to an absorbed dose of 15 kGrad gives maltohexaoses. Subsequent studies[123,124] of cyclohepta- and cyclohexa-amyloses showed that the presence of water influences the efficiency of their radiation-chemical decomposition (Table 4). The products did not contain significant concentrations of glucose or maltoheptaose. The chief products were gluconic acid lactone and maltohexaose. Similar transformations were observed in the γ-radiolysis of cyclohexa-amyloses. The products included the same lactone and maltopentaose, but not maltohexaose, which is the chief product of the acid hydrolysis of this compound.

Thus the action of ionising radiation on cycloamyloses leads to cleavage of the cyclic system. The nature of the transformations taking place in the dried substance demonstrates unambiguously the identical yields of the initial radiolysis products maltohexaose and acid on the one hand, and the yield for the decomposition of the amylose on the other. Thus the cleavage of the polysaccharide ring is accompanied by the formation of one molecule of maltohexaose and acid. It can be seen from Table 4 that the presence of water inhibits the decomposition of the polysaccharide. On drying in air at 378 K, a moisture content of about 1.5% is preserved, corresponding to a molar ratio water : substance of 1 : 1. The presence of one water molecule per molecule of the polysaccharide leads to a decrease in the decomposition yield by a factor of almost 2 (see Table 4).

The crystals of the cyclohepta-amyloses isolated from aqueous solution contain ~14.8% water; the same quantity of water is present in amylose which has been kept for a long time in air. In this case there are ten water molecules per molecule of the substance. The cyclohepta-amylose decomposition yield, calculated for the total absorbed energy, is 6.2. If however account is taken only of the energy absorbed by the polysaccharide, the yield is 7.5, as in the previous case.

From this examination it might be concluded that the radiolysis products of water (H atoms and OH radicals) do not take part in reactions with the cyclohepta-amylose; this is undoubtedly not the case, however. Their reaction is apparently not accompanied by the breakdown of the cyclic structure of the polysaccharide. The presence of water also leads to an appreciable decrease in the yield of acid compared with the yield of maltohexaose, apparently due to the participation of water in reactions with intermediate decomposition products of the polysaccharide.

A detailed chemical analysis of the final products of the radiation-chemical transformations of cycloamyloses has been carried out.[126] The data obtained confirm the previously

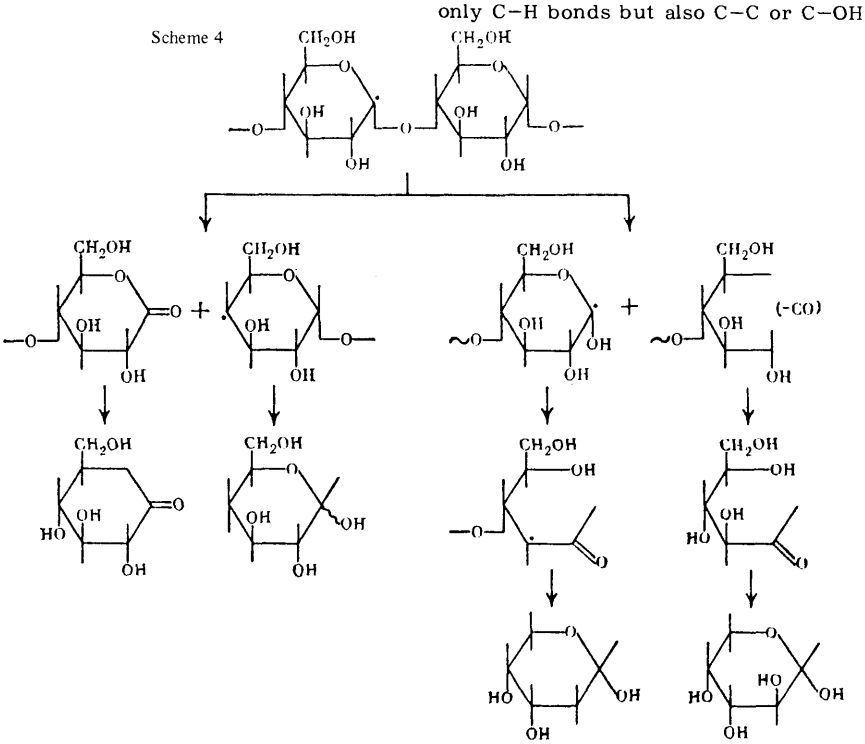
established fact[123–125] that the cleavage of the cyclic structure is the main process in cycloamyloses subjected to the action of radiation. By analogy with earlier studies of the radiolysis of simple carbohydrates,[118] it was suggested that the position of the keto-groups in the *D*-glucose residues produced in the radiolysis of the amyloses coincides with the position of the initial attack, that is with the localisation of the radical centres. These keto-groups are produced in irradiated carbohydrates as a result of the following reactions: a) disproportionation, or possibly the removal of hydrogen atoms from the α-OH group as a result of attack by primary or secondary radicals; b) radical rearrangement; c) removal of a molecule of water, alcohol, or CO; d) hydrolysis of acetal bonds if the radical centre is in an adjacent position; e) the formation of deoxy-groups as groups adjacent to keto-groups in a reaction following the addition of an H atom as a result of disproportionation.

Schemes for the radiation-chemical transformations of amyloses, proposed on the basis of these concepts, are given below.[123,124] It is assumed that the formation of the final radiolysis products is determined by the method by which the radical state is localised in the cycloamylose.

Scheme 4 illustrates chemical transformations involving radicals in which the electron density is localised on the C(1) atom [$R_{C(1)}$ radical]. Here and in subsequent schemes, the last stage corresponds to the hydrolysis of the oligosaccharides in aqueous solution to an identified monosaccharide. According to scheme 4, glucono-1,5-lactone is formed either by the hydrolysis of the glucoside bond closest to the radical centre or (preferentially) by the radical rearrangement C(1) ⇌ C(4). In the last case, electron transfer to the C(4) atom gives 4-deoxy-*D*-xylohexaose. The altered linear chain of the oligosaccharide will thus contain two functional groups at its ends, and the product will be a derivative of maltohexaose or maltoheptaose.

Other reactions involving the removal of CO and OH groups from the $R_{C(1)}$ radical have been proposed[123,124] to explain the formation of arabinose, ribose, and 2-deoxypentaose. The main product obtained according to scheme 5 is apparently *D*-arabinose.

Scheme 4



Scheme 5 shows the chemical changes in cycloamylose when the radical centre is localised on the C(4) atom [$R_{C(4)}$ radical]. The main result of the chemical transformations according to scheme 5 is the formation of 3-deoxyerythro-hexaose-4-ulose.

Table 4. Influence of the presence of water in a specimen of cyclohepta-amylose (CHA) on the yields of its radiation-chemical transformation*.[123]

Specimen	Decomposition of CHA	Formation of acid	Formation of maltohexose
Kept in air**	6.2	2.8	6.6
Kept in air at 378 K	7.4	7.5	7.5
Kept in a vacuum at 77 K	14.6	14.2	14.2
Aqueous 8×10^{-3} M solution	1.4	2.2	1.2

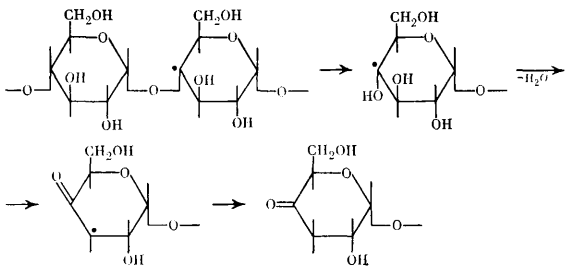
*The γ-irradiation of the specimens was carried out in a vacuum at room temperature. Dose power ~ 2.6×10^{17} eV g^{-1} min^{-1}, $D \sim 2 \times 10^{20}$ eV g^{-1}.
**The yields of H_2, CO_2, and CO were 3.1, 2.2, and 0.9 respectively.

Finally, scheme 6 reflects the possible transformations of amyloses with a reaction centre on the C(5) atom [$R_{C(5)}$ radical].

When the reaction takes place according to scheme 6, the radical rearrangement C(5) → C(1) gives a keto-group on the C(5) atom, and also a 4-deoxy-group.

A number of identified compounds do not appear in the proposed general schemes. Some of them are apparently produced as a result of the transformations of radicals with localisation of the unpaired electron, for example, on the C(6) atom, or by more complex schemes based on the less probable process of radical formation by the rupture of not only C–H bonds but also C–C or C–OH bonds.

Scheme 5

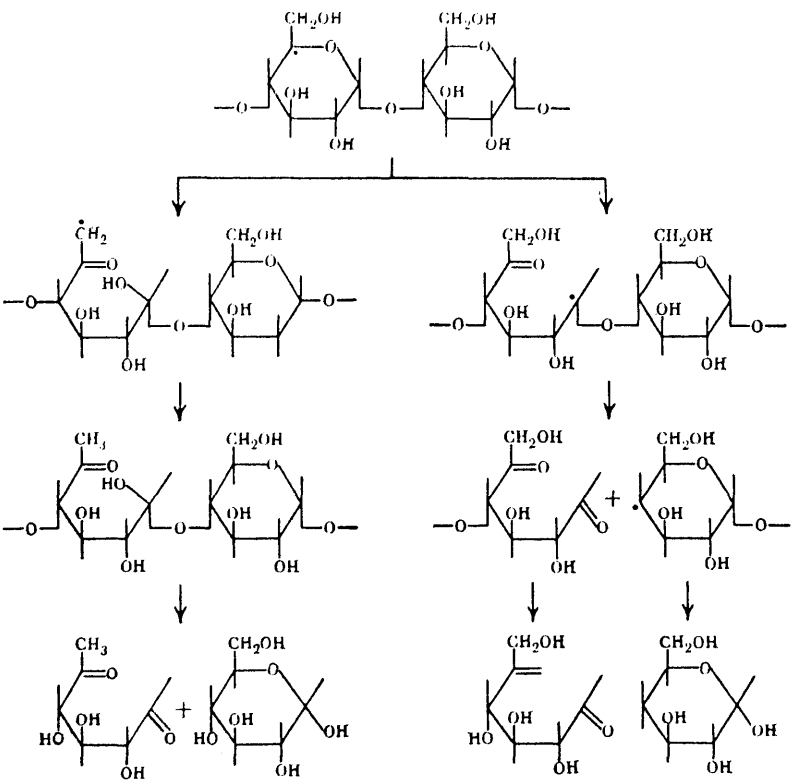


VI. MECHANISM OF THE RADIATION-CHEMICAL TRANSFORMATIONS OF CELLULOSE

The examination of data on the radiation-chemical transformation of cellulose shows that in the initial stages of the interaction with ionising radiation, free radicals are produced in the polymer, with localisation of the electron density mainly on the carbon atoms in positions 1 and 4. The subsequent degradation of the macromolecules and the formation of carbonyl and carboxyl groups and various chemical compounds, are initiated by radical species. A quantitative comparison of the yield of radicals, measured by EPR, after the γ-irradiation of cellulose at 77 K (~3.6 [71]) with the yield of its degradation (7–8, see section IV) and with the yield of carbonyl (7.6 [102]) and carboxyl (3–4 [102,119]) groups after γ-irradiation or irradiation by accelerated electrons at room temperature, shows that all these yields are of the same order of magnitude. When account is taken of the difference in the accuracies of their determination, including chemical side reactions of cellulose during the chemical analyses, and also the influence of the conditions of the irradiation on the efficiency of the radiation-chemical decomposition of cellulose, the possible partial disappearance of radicals even at 77 K, and other factors, it can apparently be concluded that each case of damage to the cellulose macromolecule with the formation of a radical centre is accompanied by subsequent bond rupture and the formation of carbonyl and carboxyl groups at the point of rupture. Allowance must also be made for the fact that it is possible in principle to have chemical transformations of cellulose involving excited states, without the formation of intermediate radical–ion products.

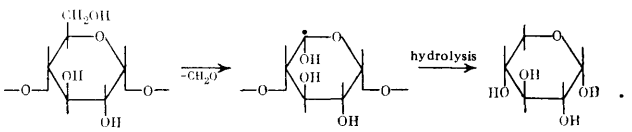
The study of the mechanism of the radiation-chemical degradation of cellulose is extremely difficult, because of the difficulty of the chemical analysis of the functional groups of the macromolecules. Considerable valuable indirect information on the main routes of the chemical transformations of cellulose initiated by reaction of radiation has been obtained by studying the final radiolysis products of model compounds, particularly cycloamyloses. Comparison of the data obtained in the analysis of the products of the acid hydrolysis of aqueous extracts of irradiated cellulose and data on the radiolysis of cycloamyloses shows unambiguously that the radiation-chemical transformations of these compounds take place by the same mechanisms.[127] For example, the final radiolysis products of cellulose, as in the case of cycloamylose, do in fact, in accordance with scheme 4, contain arabinose and 2-ketogluconic acid, and in accordance with schemes 5 and 6, various deoxy- and deoxyketo-compounds are formed.[112,119] There is not only a qualitative correspondence in the chemical reactions but also good quantitative agreement in the efficiencies of the radiation-chemical decompositions. Thus chemical analysis (Table 4) indicates that for cyclohepta-amylose dried in air, the yields for the decomposition and the formation of acid and molecular gases practically coincide with the corresponding yields for cellulose (see section V).

Scheme 6



Mention must be made of the fact, difficult to explain, that the products of the acid hydrolysis of an aqueous extract of irradiated cellulose, in addition to glucose, also contain xylose,[19] and the yields of these monosaccharides are ~49 and ~10 respectively. The formation of glucose in the acid hydrolysis of cellulose is a common phenomenon. The detection of xylose in the hydrolysate in yields comparable with the yield of glucose is extremely unusual, however. Xylose, and also arabinose, have also been detected in irradiated starch.[128]

A mechanism has been proposed for the formation of xylose.[129] It includes the rupture of the C–H bond in position 6 and the removal of formaldehyde, with the subsequent transformation of the resulting radical to give xylose:



According to this mechanism, the radiolysis of cellulose should give formaldehyde with a yield equal to the yield of xylose; it was not detected, however. Formic acid was found, however (yield 2.3).[19] It might be assumed that it is formed from formaldehyde in the acid-containing aqueous solutions during the acid hydrolysis of aqueous extracts of irradiated cellulose. Its yield is appreciably lower than that expected for the above mechanism, however. It has therefore been suggested[19,113] that formic acid appears in the oxidative degradation of glucose. Thus the scheme proposed[129] for the formation of xylose apparently has not been proved.

Malonic dialdehyde has been detected in irradiated cellulose.[19] Its yield for dry cellulose is 0.016, and in neutral and acidic aqueous solutions the yields are approximately the same and equal to $(6–7) \times 10^{-3}$. In alkaline solutions, however, there is a significant increase in the yield, to 0.256. The dependence of the yield of this product on the dose in the last case passes through a maximum at a dose of 2.5 kGrad. The formation of malonic dialdehyde has been established in the radiolysis of simple carbohydrates.[130,131]

Thus in the radiation-chemical degradation of cellulose, carbonyl and carboxyl groups are produced at the ends of the molecular fragments. The subsequent hydrolysis of these low-molecular polysaccharides gives deoxy- and deoxyketo-sugars, complex and simple organic acids, sugars, and other compounds. Dehydrogenation and degradation of the glucopyranose rings take place with the liberation of appreciable quantities of hydrogen, carbon monoxide, and carbon dioxide. Radiation changes can also take place without rupture of the polymer chain, and may be accompanied by the production of new groups (CHO, CO, COOH, etc.) in individual units.

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The analysis of data on the radiolysis of cellulose shows a fairly complex picture of radiation-chemical transformations taking place. At the present time it is possible to put forward only approximate general schemes for the mechanism of the degradation of the macromolecules and the formation of the final compounds, which are polysaccharides with various terminal groups. Subsequent studies of the radiation chemistry of this important natural polymer will make it possible to refine the mechanism of its radiolysis.

The questions which are apparently of greatest interest at present for the successful solution of a number of practical and scientific problems relating to the radiation processing of cellulose-containing materials are related to the search for methods of intensifying the degradation of cellulose and establishing the principal final products. For this purpose it is necessary to study the influence of temperature, moisture content, and various additives on the efficiency of the radiation decomposition of cellulose. The solution of these and other problems will facilitate the introduction of radiation methods into technological processes for the utilisation and processing of cellulose and cellulose-containing materials.

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Institute of Physical Chemistry,
Academy of Sciences of the USSR,
Moscow

Translated from *Uspekhi Khimii*, 53, 2078-2100 (1984) U.D.C. 543.544.25;543.544.45

Selective Detectors in Gas Chromatography

L.Ya.Gavrilina, V.I.Zheivot, and O.A.Emel'yanova

The present state of selective gas-chromatographic detection has been examined. The principles, developmental trends, and characteristic features of selective detectors of 14 types have been described briefly, and examples of their practical application have been given. Particular attention has been paid to the use of these detectors in the analysis of micro-quantities of harmful chemical compounds in environmental materials.
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I. INTRODUCTION

The recent increase in interest in highly sensitive selective detectors is related to the extension of the range of problems being solved by gas chromatography, and also to an increase in the complexity of the compositions of the mixtures being analysed. This applies particularly to the analysis of environmental materials and specimens of biological origin, where the resolving power of the most efficient gas-chromatographic columns combined with highly sensitive universal detectors is insufficient for the complete separation and determination of all the components present in a specimen.[1] At the same time, however, it is often necessary merely to know whether compounds of a given class are present. This information can be obtained using a detector which reacts selectively only to compounds of the given class. The use of selective detectors is particularly promising in the analysis of pollutants in air and water, where it is necessary to determine traces of harmful substances in the presence of large quantities of the main components.

The action of selective detectors is based on the most varied properties of the substances being analysed, such as their ability to undergo ionisation, emit (or absorb) light, undergo chemical reaction, etc. Many of these detectors are fairly simple to construct and convenient to use, and are firmly established in everyday gas-chromatographic analytical practice. Examples include the electron-capture detector, which is sensitive to halogen-containing organic substances, nitro-compounds, and other substances which act as electron acceptors; the thermo-ionic detector, which has an increased sensitivity to nitrogen-, phosphorus-, and halogen-containing compounds; the flame-photometric detector (S- and P-containing compounds); and the radiometric detector, used to detect substances labelled with radioactive isotopes.

The terms "universal" and "selective" are to some extent arbitrary when applied to detectors. Thus the universal flame-ionisation detector, which is highly sensitive to practically all organic compounds, is insensitive to most gases and vapours of inorganic substances, and the radiometric detector, selective with respect to different types of radiation, is non-selective in the sense that it cannot determine whether the labelled substance belongs to a particular class of chemical compound. A detector is usually regarded as selective if its sensitivities for substances of two different classes differ by at least an order of magnitude.[2]

The present review of the literature of the past ten years examines the present state and examples of the practical application of the most frequently employed selective gas-chromatographic detectors: flame-photometric, plasma-emission, photo-ionisation, etc.
tography has been combined with infrared and mass spectrometry and with chemical ionisation are also discussed.

II. SPECTROSCOPIC DETECTORS

1. The Flame-photometric Detector

The action of the flame-photometric detector (FPD) is based on the recording of the emission spectra produced by the thermal heating of the specimen in a burner flame.[1,3-24] A hydrogen–air flame with added oxygen is usually employed. The combustion of substances whose molecules contain atoms of sulphur, phosphorus, nitrogen, selenium, tin, and various other elements gives excited species (for example S_2^*, HPO^*, etc.), which emit a characteristic spectrum.[1,3]

The design of the FPD combines the cell of a flame-ionisation detector (FID) with an optical scheme for measuring the light flux.[3] The flame of the FPD is richer in hydrogen than that of the FID. The conditions of mixing of the streams of carrier gas and auxiliary gases in the burner, and their total consumption, influence the sensitivity and stability of operation of the FPD. The optimum conditions may therefore be different for different versions of this detector.[1,3-7] To prevent overheating of the optics and sensitive elements, the flame is enclosed in a quartz or Pyrex tube, or light pipes may be used. The background emission of the flame is absorbed by interference filters, which transmit only light of the required wavelength (λ = 394 nm for sulphur compounds, and λ = 526 nm for phosphorus compounds). The sensitivity and selectivity of the FPD with respect to a given substance are determined by the intensity of the analytical line in the

spectrum and the width of the transmission band of the light filter. The use of filters with narrower transmission bands increases the selectivity and the useful signal : noise ratio, but decreases sharply the sensitivity of the FPD, since the intensity of the light flux is proportional to the square of the transmitted band width.

The flame-photometric detector is a flow detector. For phosphorus compounds, the magnitude of the signal (the area of the peak) is directly proportional to the flux of the substance.[3] For sulphur compounds, this relationship is logarithmic; the exponent in the equation relating the area of the peak to the mass velocity of the substance being analysed in the detector should theoretically be equal to 2, but in practice it takes values from 1 to 2.5 for different substances; this is due to the fact that excited species S_n^* may be formed in the detector flame in addition to the species S_2^*.[6,9]

The sensitivity threshold of the FPD is $(2-100) \times 10^{-12}$ g s^{-1} for phosphorus compounds,[3,4,6,7] and $(6-300) \times 10^{-12}$ g s^{-1} for sulphur compounds.[4-6,10] This corresponds to approximately 10^{-9} g of the element being determined in the specimen.[7] The sensitivity of the determination of substances containing nitrogen, boron, tin, and other elements is slightly lower.

The linear range of the FPD is 10^4-10^5 for phosphorus compounds,[3,7] but is much lower ($\sim 10^2$) for sulphur compounds.[6,11] It has been proposed that the linear range of operation of the FPD in the analysis of sulphur compounds be increased by adding traces of carbon disulphide vapour (2–4 mg s^{-1}) to the carrier-gas stream[6] or by treating the detector connections with sulphur compounds.[10] This also leads to a decrease in the detectable minimum.[12] The sensitivity of the FPD with respect to sulphur-containing compounds is 10^4-10^7 times greater than that with respect to hydrocarbons and alcohols, and depends on the ratio of the gas flow velocities and on the design of the detector.[13] A slight decrease has been observed, however, in the magnitude of the signal for sulphur compounds, when eluted from the gas-chromatographic column together with hydrocarbons. The different extent of the decrease in the sensitivity of the FPD with respect to sulphur and selenium compounds, difficult to separate, when methane is added to the carrier gas has been used to identify these substances when present together.[12]

The high selectivity and sensitivity of the FPD have enabled it to be used to determine traces of thiols and organic sulphides in air,[14] isopropyl methylphosphonofluoridate (Sarin)[15] and butyltin[16] in water, sulphur-containing pesticides in wheat,[17] and various sulphur compounds in specimens of soil and air in regions of petroleum discharge or spillage.[18,19]

In the quantitative analysis of micro-quantities of sulphur compounds, difficulties arise as a result of the tendency of these substances to undergo irreversible sorption in the connections, and also the fact that the molar signal of the FPD depends on many factors, so that special calibration is required.[24] As shown for the analysis of dipropyl sulphide using the "Meloy Laboratories" 100 AT FPD,[9] the magnitude of the detector signal depends on the nature of the solvent, the number of successive analyses, and the duration of the intervals between analyses; for low concentrations, the difference in the magnitude of the signal may reach 200%. It is recommended[9] that the FPD should be used for the quantitative determination of organosulphur compounds at concentrations not lower than 10^{-4} g ml^{-1}. The accuracy of the determination of traces of hydrogen sulphide in the concentration range $10^{-4}-10^{-7}$ vol.% using the FPD produced by the Dzerzhinskii Special Design Office, with preliminary concentration, has been confirmed.[20] These detectors show "memory effects", which are stronger, the lower the concentration of the trace component. To obtain results with a mean-square deviation of ±10%, thorough purification of all the gases and prolonged flushing of the gas lines of the chromatograph and the connections through which the specimen is passed are required. If various precautions are taken, the FPD can be used for the quantitative determination of the concentrations of carbonyl sulphide, hydrogen sulphide, and sulphur dioxide at the level of $10^{-2}-10^{-7}$ mass % with a standard deviation of 7–5%.[21]

2. The Chemiluminescent Detector

Chemiluminescent detectors (CLD) record the luminescence spectra of the products of the chemical reaction of the substances being analysed and the reagents ozone[25-32] or atomic oxygen,[33] supplied continuously to the detector. The spectra are recorded using photomultipliers and photon counters; monochromators and electronic noise filters are also used.[27]

Luminescence is shown by the products of the reaction of ozone (or atomic oxygen) with alkenes,[28,33] sulphur dioxide[28,29] and nitric oxide. The analysis of nitrogen-containing compounds involves their thermal decomposition to give nitric oxide, which is then oxidised by ozone to excited nitrogen dioxide, which gives a luminescence spectrum. It is considered[33] that the method using atomic oxygen is more selective than that using the reactions of the substance being analysed with ozone.

The sensitivity threshold of the CLD is $\sim 10^{-9}$ g s^{-1}, and the linear range is 10^4. The detection limit for alkenes can be lowered by a factor of 200 by adding to the carrier gas traces of carbon disulphide or hydrogen sulphide, which undergo intermediate radical reactions and facilitate the reaction of the alkenes with ozone.[28]

The chemiluminescent detector has been used to determine the concentration of trimethylamine in air,[26] nitrosamines in the environment,[27,30,31] unsaturated hydrocarbons in industrial atmospheres,[33] and sulphur dioxide[29] and other substances in the troposphere and stratosphere. Many of these substances cause breakdown of the ozone layer and smog formation.[32] The simultaneous recording of chromatograms using a chemiluminescent detector and a universal detector (for example the FID) makes possible the group analysis of the concentrations of paraffins and aromatic hydrocarbons.[33]

3. The Plasma-emission Detector

Plasma-emission detectors (PED) record the emission from excited atoms and recombined diatomic fragments, obtained by the decomposition of the molecules of the compounds being analysed with a high-temperature helium or argon plasma.[4,34-43] The plasma, with a temperature of 4000–10000 K, consisting chiefly of the ionised gas, is formed either directly in a direct-current arc or by induction heating of the gas in the electromagnetic field of a high-frequency generator.[36] The excitation of the atoms and molecules of the substances being analysed may take place under the influence of electron impact, and also in collisions with metastable argon or helium atoms. The use of helium is preferred, since it has a simpler photon background spectrum and its metastable atoms have a higher energy.

The PED is now used to determine up to 30 elements in organic compounds, including non-metals difficult to excite, such as C, N, O, F, etc. The selectivity of this multi-element detector is achieved by tuning the spectrograph to the zero line of the spectrum by means of a monochromator, and by correction for the background.[36,39] Thus the chromatogram of petrol, recorded at $\lambda = 279.83$ nm (manganese line),

gave only the peak of the tricarbonylcyclopentadienyl-manganese present. The use of multi-channel PED appears promising, particularly for elemental analysis, since the molar signal of this detector is proportional to the number of atoms of the given element in the molecule of the substance being analysed, and is practically independent of the type of functional group.[36]

The discharge is usually produced in a thick-walled quartz capillary tube (internal diameter 0.5–1 mm). The carrier gas from the column and an additional stream of the same gas (0.05–6 litre min^{-1}) are supplied to the tube. The optimum ratios of the velocities of these two streams, and their overall velocity, are different for different elements.[36,41] Models of this detector operating at atmospheric pressure and at a reduced pressure have been described. The detector operating at atmospheric pressure is preferable, since direct axial observation of the plasma emission is possible (and not observation through the wall of the discharge tube, which introduces additional distortion).[41] It is useful to place a valve or a four-way tap with an additional gas-chromatographic detector between the column and the PED, to remove solvent from the specimen and avoid overloading the plasma with it.[35]

These detectors are promising for the analysis of specimens taken from the environment. The small internal volume of the detectors has made it possible to use them with capillary gas-chromatographic columns.[37,41] They have been used to determine traces of organic compounds of lead, silicon,[42,43] mercury, selenium, arsenic,[36] boron,[40] and fluorine[39] in water, air, soil, and various food products using specimens containing 10–600 pg of the substance being analysed. The selectivity of the determination of these elements relative to carbon varies from 70 to 360000; the linear dynamic range of operation of the detector is 10^2–10^3, and the reproducibility of the results when the operating conditions are strictly observed is 1–5%.[41,43]

4. The Combination of Gas Chromatography and Infrared Spectroscopy

Absorption infrared spectroscopy, combined with gas chromatography, is used for the qualitative identification of substances from their absorption spectra in the infrared range.[44] Continuous analyses are carried out by combining the gas chromatograph with an infrared spectrometer in which rapid scanning of the spectrum is carried out. Extensive use has been made of Fourier transform infrared spectroscopy[1,45–50] where a computer is used to store data on the intensity of absorption at different wavelengths and then substract the background. The complete spectrum or chromatogram is then reproduced by summation of the intensities of absorption of the compound being analysed, either throughout the entire spectrum or in a selected part of it.

The resolving power of fast-acting infrared spectrometers is lower than that of the ordinary instruments,[49] but the possibility of rapidly obtaining comparative data on the magnitude of the light absorption by the substances being analysed in the selected range of the spectrum makes this method extremely selective. There are at least five specific "windows" in the infrared spectrum, characteristic of five classes of compound: for example, the ranges 2930–3000 cm^{-1} for alkyl derivatives of benzene,[49] and 700–900 cm^{-1} for polyaromatic hydrocarbons.[47] The sensitivity of the determination and the useful signal : noise ratio are increased considerably if the chromatogram is reproduced from the intensity of the absorption in the range of the spectrum specific for the given class of compound.[47,49] Thus Fourier transform infrared spectroscopy can be used for the group analysis of various compounds in complex mixtures. Quantitative analysis by this method has also been reported, but the linear range of operation is very short (less than an order of magnitude). The minimum detectable quantity of pyrene in a specimen of the aromatic fraction of crude petroleum was 710 ng.[47]

New attachments and connecting units are being developed, which make it possible to work even with small-capacity capillary columns without loss of efficiency.[1,46–48,50] The device proposed in Ref. 47 consists of a gold-plated twelve-face copper receiver, placed in an evacuated (~10^{-6} mmHg) and cooled (to 17 K) compartment, to which the substance from the column is supplied through a heated glass-lined steel capillary. As the receiver is rotated, the fractions of the substance are deposited in turn on its faces; the absorption spectra of the trapped fractions are recorded at the moment when the corresponding faces pass in front of the spectrometer objective. The carrier gas (99.999% pure nitrogen) is not frozen under these conditions.

5. The Fluorimetric Detector

The action of the fluorimetric detector is based on the ability of various substances to fluoresce when irradiated or heated.[24,44,51–54] The intensity of the fluorescence is measured using a spectrofluorimeter. Since very few substances fluoresce, this method is highly selective, and is used in combination with all forms of chromatography, including gas chromatography. Methods are available, for example, for determining traces of anthracene, chrysene, and benz-α-pyrene in the atmosphere.[52] The selectivity of this method can be controlled by choosing an appropriate radiation source. Detectors have been described for the analysis of traces of nitrogen dioxide[53] and other substances[54] in air, based on the use of their long-wave fluorescence, induced by laser irradiation. The detection limit for nitrogen dioxide was 6×10^{-5}% (without preliminary concentration). Preliminary freezing of the traces of nitrogen dioxide made it possible to lower the detection limit to 2×10^{-6}% (preliminary gas-chromatographic separation was not used). The minimum detectable quantity of sulphur-containing gases is 100 ng.[24]

6. The Atomic-absorption Detector

Atomic-absorption spectroscopy, developed initially for the analysis of metals in inorganic materials,[55] has recently been used increasingly, combined with gas chromatography, in the analysis of organometallic compounds.[56–61] Dissociation of the molecules of the substances being analysed to atoms and absorption by the latter of the light from a standard source take place in the flame (or in a heated graphite cell). The light source usually consists of a special lamp in which the cathode is made of the metal which is being determined. The use of light sources with a line emission spectrum, in which the width of the lines is smaller than the width of the lines of the spectrum excited (~10^{-2} nm), makes this method exceptionally selective; the use of a monochromator (spectrophotometer) is necessary, to increase the signal : noise ratio.[55] The absorption spectra of most elements, obtained in an atomic-absorption spectrometer, are exceptionally simple, since they contain only the resonance lines corresponding to absorption transitions from the ground levels.

The atomic-absorption detector has been used for the gas-chromatographic analysis of organic manganese carbonyl in air,[56] tetra-alkyllead,[58] metal chelates (chromium, iron, copper, and cobalt[59]), and organometallic compounds of gallium, indium,[57] tin,[60] and lead.[61]

The minimum detectable quantity of substance, calculated as the metal, corresponds to several nanograms in the specimen, and can be improved by preliminary concentration.[61] The necessary precautions are for the most part those characteristic of work with organometallic compounds.

III. IONISATION DETECTORS

1. The Photo-ionisation Detector

A large number of recently published papers describe the study and application of photo-ionisation detectors (PID) in gas chromatography.[1,2,4,62-76] This detector has been known for a long time,[4,62] but its construction was insufficiently convenient. The new version can be readily connected to a gas-chromatographic system, including a portable gas chromatograph, and it promises to become a standard detector for gas chromatography.[65]

The action of the PID is based on the ionisation of the molecules of the substances being analysed under the influence of ultraviolet radiation, and the recording of the resulting ion current. The sources of ultraviolet radiation which have been tested include helium (20.2 eV) and argon (11.7 eV) discharge lamps without windows,[63] hydrogen lamps with different windows transmitting quanta with energies of 9.5, 10.2, and 11.7 eV,[64,65,75] and dye lasers.[71] The use of discharge lamps without windows had the disadvantage that it was necessary to maintain a vacuum at the outlet from the chromatographic column. The most widely used source is a hydrogen lamp (10.2 eV) with an MgF_2 window, placed inside the ionisation compartment of the detector.

Unlike the flame-ionisation detector, which is destructive and requires the use of three gases (hydrogen, air, and an inert carrier gas), the PID is not destructive, since the ions recombine on the cathode and are blown from the detector; the PID requires only one carrier gas,[65,72] preferably argon or helium.[69]

The PID is a concentration detector; the areas of the peaks decrease sharply (almost exponentially[62]) with increase in the velocity of the carrier-gas stream; the optimum velocities lie below 10 ml min^{-1}, so that it appears promising to use PID combined with capillary columns, particularly when the radiation sources used are lasers, which make it possible to decrease considerably the volume of the detector.[71] The internal volume of a PID with a hydrogen lamp can be reduced to ~50 μl.[72-74] The efficiency of a system consisting of a capillary column with this PID is only 10% lower than that of a similar system with an FID. Its main characteristics (magnitude of the linear range, noise level, background current, and sensitivity) are comparable with those of the FID, and it is superior to the latter in its sensitivity to aromatic hydrocarbons.[63,72]

Under the influence of ultraviolet radiation, photochemical reactions take place in the photo-ionisation detector, and the following reactions can be regarded as the most important in the production of the signal in this detector.[77-82]

1. The primary photo-transformation — the absorption of a quantum of energy and the conversion of the molecules to the excited state.

2. The secondary reactions of the excited molecules: a) interconversion and triplet formation; b) photo-ionisation (removal of an electron and the formation of an ion pair); c) photo-decomposition (photolysis to give radicals or ions); d) photo-sensitisation (the breakdown of non-excited molecules to radicals or ions as a result of collision with excited sensitiser molecules); e) two-photon decomposition or ionisation; and f) photo-addition (photo-oxidation, photo-hydrolysis).

The probability and rate of a given reaction are determined by the energy of the photons of the excitation source, the structure and properties of the substances being analysed, and the conditions in the reactor (pressure, concentration of the substance, temperature, the presence of other substances, the flow velocity, etc.). If the energy of the exciting photons is greater than the ionisation potential of the substance being analysed, the most probable reaction is photo-ionisation, and it can be stated that this substance can be detected. In those cases where the ionisation potential of the substance is lower than the energy of the quanta, it may still be detected, although with a lower sensitivity, as a result of other reactions, for example reactions (d) and (e), whose probabilities depend on such characteristics of the molecules of the substance as the difference between the energies of the singlet (or triplet) excited levels and the energy of the ground singlet level, and the lifetime of possible triplet excited states. The Table gives as an example the values of the first adiabatic ionisation potentials and the characteristics of the excited states of various molecules. More extensive data can be found in the literature,[83-85] and also in Ref. 86, which gives the ionisation potentials for 500 organic substances.

Table. Values of the first adiabatic ionisation potential (IP), the excitation energies of the singlet (E^S) and triplet (E^t) states above the energy of the ground state, and the lifetimes of the triplets (τ) of various substances.[77,83-85,87-89]

Substance	IP, eV	E^t, eV	τ, s	E^S, eV
Methane	12.99	—	—	—
Ethane	11.65	—	—	9.15*
n-Butane	10.63	—	—	—
n-Pentane	10.35	—	—	—
n-Hexane	10.17	—	—	—
Ethylene	10.516	—	—	7.6*
But-1-ene	9.57	—	—	—
Methanol	10.85	—	—	6.9*
Ethanol	10.48	—	—	6.7
Acetone	9.69	3.38	10^{-3}	3.64
Acetonitrile	12.21	—	—	7.3*
Benzene	9.25	3.64	7	—
Phenol	8.50	3.53	—	—
Biphenyl	8.27	2.82	3.1	4.1
Naphthalene	—	2.64	2.3	3.9
Carbon tetrachloride	11.47	—	—	—
Water	12.59	4.76; 9.43	—	7.4
Oxygen	12.06	0.98**	0.05**	3—4*
Nitrogen	12.56	—	—	—
Nitrogen dioxide	12.3	—	—	—
Carbon dioxide	13.79	—	—	—
Sulphur dioxide	12.34	—	—	—

*For these substances, the values of E^S were estimated in the present work from the values of λ_{max} for the most intense absorption band in the ultraviolet range.[83-85]
**The energy and lifetime of the lowest excited singlet state are given (since the ground state is a triplet state).

A detector in which the lamp gives radiation with an energy of the quantum $h\nu$ = 20.2 eV is practically universal, and is used for the analysis of inert gases and all organic substances. A detector with a lamp for which $h\nu$ = 11.7 eV already shows some selectivity; it is not sensitive to simple gases, and gives a signal from aromatic hydrocarbons which is ~30% more intense than that from alkanes with the same

number of carbon atoms.[63] A higher selectivity is shown by detectors with lamps for which $h\nu = 10.2$ eV and $h\nu = 9.5$ eV. A detector with a lamp for which $h\nu = 10.2$ eV is not sensitive to simple gases and C_1–C_4 alkanes. C_5 and higher saturated hydrocarbons give a signal, but the sensitivity of the detector with respect to these compounds is lower than that for unsaturated and aromatic hydrocarbons. This behaviour of the detector is due to the high efficiency of the ionisation (that is the quantum yield of the photo-reaction) of compounds with a π-bond, whose electrons are localised to a much greater extent than the electrons of a mobile σ-bond.[63]

The relative molar sensitivity of the most widely encountered PID ($h\nu = 10.2$ eV) for n-alkanes (standard benzene) increases with increase in the number of carbon atoms, and that for polyaromatic compounds increases with increase in the number of benzene rings. It is greater for cyclic compounds and iso-alkanes than for the non-branched compounds. In general, for a given number of carbon atoms, the relative molar sensitivity increases in the order: n-alkanes < primary alcohols ≤ ethers < aldehydes < ketones. For substituted benzenes, electron-acceptor substituents decrease the sensitivity of the determination, and electron-donor substituents increase it.[68,69]

The fact that the relative molar sensitivity of the PID increases to a greater extent with increase in the number of π-bonds, particularly when conjugated, in the hydrocarbon molecule, compared with the increase in the number of carbon atoms has been used in a number of studies for the group identification of alkanes, alkenes, and aromatic hydrocarbons in mixtures,[63,70] and of phenols in car exhaust gases.[76] The substance at the outlet from the chromatograph is recorded simultaneously by two detectors, a PID and a universal FID, and their signals are compared. An equation has been proposed,[70] relating the ratio of the values of the normalised signals of these two detectors to the number of carbon atoms in the molecule of the substance, its ionisation potential, the number of electrons ionised in the molecule, and the energy of the photons. The experimental data almost always show sufficiently good agreement with the calculated results.

A photo-ionisation detector with interchangeable lamps has also been proposed, giving radiation with an energy of the quantum of 9.5 eV, 10.2 eV, and 11.7 eV; the lamp with $h\nu = 11.7$ eV can fulfil the role of FID.[75] Replacement of the lamps does not involve breakdown of the connections between the outlet from the column and the detector, and this is particularly important when working with brittle glass capillary columns. The ratio of the values of the normalised signals obtained with lamps with $h\nu = 9.5$ eV and 10.2 eV to the signals with the lamp with $h\nu = 11.7$ eV has been used to identify alkanes and aromatic and polyaromatic hydrocarbons in complex mixtures derived from petroleum, at the level of nanogram quantities. The higher selectivity of the PID with the lamp with $h\nu = 9.5$ eV with respect to polyaromatic hydrocarbons has been emphasised.[75]

The change in the sensitivity of the analysis of aromatic and aliphatic pesticides on going from the lamp with $h\nu = 9.5$ eV to the lamp with $h\nu = 10.2$ eV has also been used for their group identification in complex mixtures.[64]

The use as radiation source of a pulse laser emitting in the wavelength range 270–335 nm, which ensures the two-photon ionisation of substances which tend to form triplets (in particular naphthalene derivatives), has made possible the selective detection of these compounds.[71] The total energy of the two photons in the wavelength range indicated is 7.4–9.2 eV. By tuning the laser to a definite wavelength, it was possible to obtain the peak of only one substance on the chromatograms; the minimum detectable quantity was 10 pg. These chromatograms are shown in Fig. 1.

The choice of the solvent for the specimens being analysed is of considerable importance when working with PID, particularly in the determination of micro-quantities using preliminary concentration and extraction. The chief requirement which must be satisfied by the solvent is transparency in the wavelength range corresponding to the lamp used — a condition which is satisfied for substances with high values of the ionisation potentials and high energy levels of the excited states. Thus acetone, hexane, and aromatic hydrocarbons cannot be used as solvent when working with a PID with $h\nu = 10.2$ eV, since the background current which they give is too high. Only carbon tetrachloride has been found to be suitable for the analysis of chlorobenzenes in air and in human blood and urine using this PID.[67] Other workers,[63] who also used a PID with $h\nu = 10.2$ eV, used acteonitrile and spectroscopically pure methanol to extract pesticides concentrated on active carbon. Acetone has been used as solvent for the specimens in work with a laser source (3.7–4.6 eV), although it gave a peak due to possible multi-photon ionisation.[71]

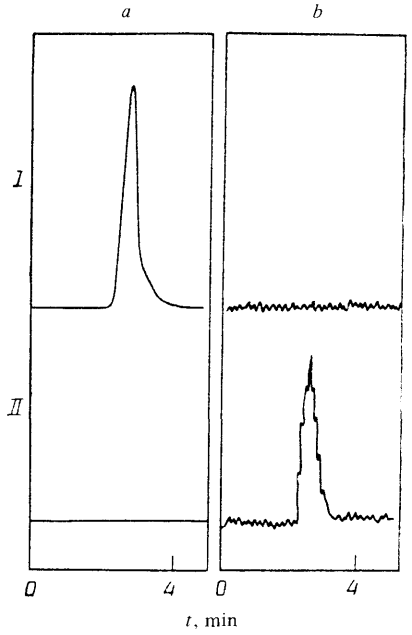


Figure 1. Chromatograms of anthracene (I) and phenanthrene (II), obtained using a PID with tunable selectivity at laser source wavelengths of 310.0 nm (*a*) and 285.0 nm (*b*). 1.3 m × 3 mm column containing 3% OV-17 on 80–100 mesh Chromosorb W; carrier-gas velocity (argon + methane in the ratio 90 : 10) 20 ml min^{-1}.[71]

The authors cited do not discuss the question of the behaviour of water in a PID. This question requires special study, since the sensitivity of gas-chromatographic detectors to water is a very important characteristic in the analysis of aqueous solutions and specimens of polluted air, water, and other environmental materials. The ionisation potential of water is greater than the energy of the quanta of the hydrogen lamps used in the PID (see Table), so that direct ionisation of its molecules is unlikely. Data have been published,

however, indicating considerable absorption by water in the ultraviolet range at 186–143 nm (6.67–8.67 eV) and 143–124 nm (8.67–10.00 eV) and the existence of a whole series of excited singlet and triplet states of its molecule.[87–89] The excited water molecules can sensitise the ionisation of other substances, eluted with it from a gas-chromatographic column. Many of these excited states of the water molecule are dissociative, and are accompanied by its breakdown to give chemically active radicals OH, H, and O, which can react with the molecules of other substances to form ions. The formation of charged and uncharged fragments of the water molecule is also possible as a result of its capture of electrons present inside the PID. All this can lead to a change in the sensitivity of the PID and an increase in its background signal at the moment when the water peak appears. Another important feature may be the deleterious influence of water vapour on the lamp window, particularly at high temperatures.

2. The Surface-ionisation Detector

The operation of the highly selective surface-ionisation detector (SID), first developed in the Soviet Union,[4,91] is based on the phenomenon of the ionisation of the molecules during their thermal desorption from a surface.

When organic substances are adsorbed on the surface of many metals, both reversible (multi-layer) adsorption and irreversible adsorption (chemisorption) take place. At high temperatures, the reversible adsorption is slight, whereas chemisorption increases with increase in temperature and with increase in the specific surface of the metal.[92] The desorption of chemisorbed molecules is often completed by their degradation, and the charge state of the species removed is determined by the nature of the charge distribution between the adsorbed molecule and the surface of the solid. For most substances, positive ions are formed.[91]

The most effective thermo-emitters for the ions of organic compounds are oxidised tungsten, molybdenum, nickel, and Nichrome, and non-oxidised tungsten, molybdenum, nickel, rhenium, and iridium. Mass spectrometry has been used to study the ability of substances of different classes to undergo surface ionisation, and the regular features of ion formation; at temperatures of 340–375 °C, amines, hydrazines, and some of their derivatives ionise readily; phosphines, arsines, and various oxygen-containing compounds (phenols, organic acids, and substances containing the benzoyl group) ionise less readily.[91,93]

Unlike many other selective detectors, the SID is selective not with respect to a heteroatom but with respect to a functional group on a heteroatom.[94] This provides the basis for the functional gas-chromatographic analysis of nitrogen-containing compounds, which involves the determination of the ratio of the heights of the peaks of each substance when chromatograms are recorded simultaneously using two parallel detectors: SID and FID. The study of 23 amines[95,96] showed that this ratio varies from 4 to 12 for primary amines, from 30 to ~300 for secondary amines, and from 700 to 6000 for tertiary amines. The existence of this clearly defined relationship between the ratio of the signals of these detectors and the type of amino-group made it possible to recommend this method for identifying amines. It is of course possible to have cases where the values of this ratio are similar for amines from different groups, but these substances generally have markedly different gas-chromatographic retention characteristics, and this is also taken into account in the identification. The selectivity of the SID with respect to amines is illustrated in Fig. 2. The SID also records the amides of carboxylic acids,[95,96] but with a lower sensitivity than in the case of the corresponding amines. The minimum detectable level is ~5×10^{-15} g s^{-1} (with respect to triethylamine), and the linear range is ~10^4–10^8. The selectivity with respect to hydrocarbons is ~10^5–10^8.[91]

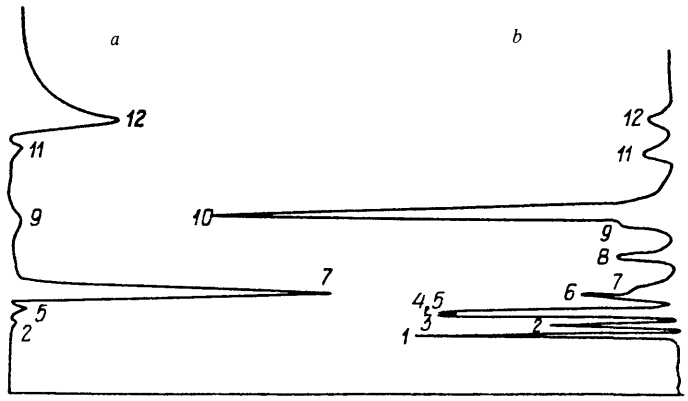


Figure 2. Chromatograms of a mixture of organic substances, obtained using an SID (*a*) and an FID (*b*) on a column containing PEG-1000 at 100 °C; emitter temperature 370 °C, velocity of air through the SID 75 ml min^{-1}. The stream of carrier gas (helium) from the column, 30 ml min^{-1}, was divided in the ratio 3:7 for the SID and the FID respectively; peaks on the chromatograms: *1*) diethyl ether, *2*) n-propylamine, *3*) methyl ethyl ketone, *4*) benzene, *5*) n-propylisobutylamine, *6*) isobutyl acetate, *7*) dipropyl-n-butylamine, *8*) di-isobutyl sulphide, *9*) pyridine, *10*) chlorobenzene, *11*) morpholine, *12*) methyl-n-octylamine, amplifier scale 1.9 × 10^{-8} A (*a*) and 10^{-10} A (*b*).[95]

The high sensitivity and selectivity of the SID make it possible to recommend it for the analysis of traces of various compounds with heteroatoms of the Va sub-group in air and other environmental materials. In general, it can be used for the analysis of substances which can be converted into amines.[91]

3. The Thermo-ionic Detector

The thermo-ionic detector (TID) was based on the flame-ionisation detector, and is familiar as a selective detector for phosphorus-, nitrogen-, and halogen-containing compounds.[1–4,23,44] Its action is based on the sharp increase in the rate of the ionisation of these substances in the presence of alkali metal vapour, so that it is sometimes called the "alkali" FID. The alkali metal salt is used in the form of a deposited layer or in the form of beads or a coating of a melt of the salt with quartz or a ceramic on a suitable holder, which are heated by a burner flame or electrically; the salt can also be introduced into the flame in the form of an aerosol.[97]

Single-flame and double-flame TID are used. In the latter, the lower part, which operates as an ordinary FID, is separated from the upper part by a grid covered with the alkali

metal salt. The products of combustion and ionisation from the lower compartment, after recombination, pass together with the alkali metal vapour into the zone of the flame of the upper burner, where specific ionisation of the molecules and fragments containing nitrogen, phosphorus, and halogen atoms takes place. Comparison of the chromatograms obtained simultaneously from the upper and lower compartments makes it possible to detect these substances in the mixtures being analysed.[3,4]

The mechanism of the ionisation in thermo-ionic detection is complex, and has not yet been fully studied. Depending on the design characteristics and operating conditions of the detector, the ionisation may take place preferentially either in the vapour phase as a result of collisions of the molecules of the substances being analysed or their fragments with the alkali metal atoms, or on the surface of an activator containing this metal. In the last case, the most important characteristics are the electronic work function and the temperature of the activator surface, and also the composition of the gaseous medium.[98]

The mechanism of surface ionisation has been realised in new TID models.[98–102] In the double-flame TID described in Refs. 99 and 100, ion formation takes place on a thermo-cathode made of platinum, nickel, or stainless steel (the cathode does not contain added alkali metal, and it is heated by the flame of the upper burner). The optimum cathode temperature is established by studying the dependence of the sensitivity of the detector on the rate of supply of hydrogen and air to the upper and lower burners. The double-flame TID is 10^2–10^3 times more sensitive than the ordinary TID. The sensitivity with respect to acetonitrile and methylene chloride is 8×10^{-10} g s^{-1} with a linear range of 10^3 and a selectivity with respect to hydrocarbons of 10^4. This detector has a simple design, its operation is stable, and it can be used in a standard chromatograph (in particular, the Tsvet-104 chromatograph).

Patterson and coworkers[1,98,102] proposed a flameless TID, which operates at low hydrogen concentrations, insufficient to support a flame, or in an inert gas (nitrogen) atmosphere. The electrically heated thermo-cathode consists of a rod with a ceramic covering containing a caesium compound; it is surrounded by a cylindrical ion collector. This TID shows a selective sensitivity with respect to nitrogen- and phosphorus-containing compounds (Fig. 3), depending on the concentration of the alkali metal on the surface of the thermo-electrode, its temperature, and the composition of the surrounding gas. At a temperature of 600–800 °C, selectivity is not observed; under these conditions, the source apparently becomes sufficiently hot for the formation of chemically active hydroxyl, hydrogen, and oxygen radicals, which may undergo ionic reactions on the surface and facilitate the ionisation of a large number of substances. The flameless TID has been used to identify environmental pollutants such as parathion (thiophos), methylparathion, malathion, nitrophenols, nitroglycerine, and other nitro-compounds. The minimum detectable quantity of nitrogen- and phosphorus-containing compounds is 10^{-14}–10^{-13} g s^{-1}, calculated for the heteroatom, with a selectivity with respect to hydrocarbons of 10^5; the linear range is 10^4–10^5.[98]

An apparatus and procedure for regulating the sensitivity of the TID with respect to substances of different classes by means of a displacement potential applied to the activator containing the alkali metal have been proposed.[102] The magnitude of the applied voltage determines the sign of the ions formed, which are collected by the collector (the burner jet acts as the second electrode; the activator is placed between the burner and the ion collector). The dependence of the magnitude of the TID signal on the displacement potential has been given for compounds of nitrogen, sulphur, phosphorus, and iodine. At definite values of the displacement potential, characteristic for each heteroatom, it is possible to take the signals of the corresponding substances from the chromatogram and hence to identify these substances. It is possible to record simultaneously chromatograms with and without the displacement potential.

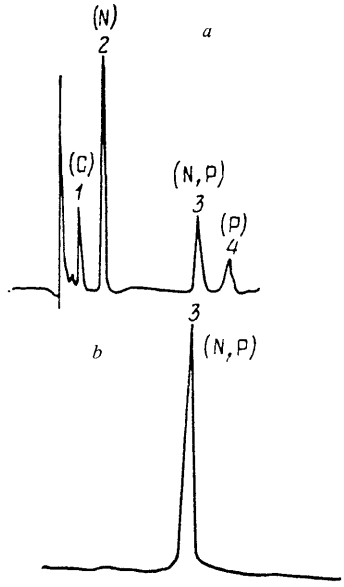


Figure 3. Comparison of the chromatograms of a mixture containing 4000 ng μl^{-1} heptadecane (*1*), 2 ng μl^{-1} azobenzene (*2*), 2 ng μl^{-1} methylparathion (*3*), and 4 ng μl^{-1} malathion (*4*) in iso-octane, obtained using a TID with a low (*a*) and with a high (*b*) concentration of caesium on the surface of the thermo-electrode in a hydrogen atmosphere containing air (*a*) and nitrogen (*b*); amplifier scale 128×10^{-12} A (*a*) and 16×10^{-11} A (*b*).[98]

The high selectivity and sensitivity of the TID, and the relative simplicity of its use, are leading to the extensive application of this detector in the analysis of micro-quantities of many harmful substances in natural materials. Methods have been described for the analysis of nitrogen-containing compounds and ammonia,[103] symmetrical triazines,[104] nitrosamines,[105] and derivatives of thiocarbamic acid.[106]

The sensitivity of the TID with respect to water has been studied;[99] although water itself does not give a signal, it decreases the sensitivity of the determination of other substances. In particular, the magnitude of the signal from a double-flame TID due to acetonitrile in the analysis of aqueous solutions was only half that in the analysis of alcoholic solutions. This was attributed[99] to a decrease in the temperature of the surface ionisation electrode.

4. The Electrical-conductivity Detector

The operation of the electrical-conductivity detector (ECD) is based on the decomposition of the substances being analysed to give ionogenic products; absorption and dissociation of these products then take place in a stream of water or other solvent, and the electrical conductivity of the resulting solution is measured continuously.[1,4,107] The decomposition of the substances can be carried out in an oxidising medium (by heating in oxygen or in air, by passing over heated copper oxide, etc.) or by heating in a stream of hydrogen in the presence of a catalyst. Organic substances containing sulphur, halogen, and nitrogen atoms in the oxidising version give mixtures $CO + CO_2$, $SO_2 + SO_3$, NO_x, HX, and H_2O, and in the reducing version NH_3, H_2S, HCl, CH_4, and H_2O.[108,110]

If conditions are created for dissolving carbon dioxide (oxidising version), the ECD operates as a universal detector. In this case the signal is proportional to the number of carbon atoms in the molecule of the substance being analysed. This detector is particularly convenient for chromatography in a stream of water vapour.[109] It is also possible to create conditions under which the measuring part of the detector contains only one of the above products, and the ECD then becomes exceptionally selective. Work in recent years has been devoted mainly to improving the selective version of this detector.[1,111–115]

The Hall detectors (Tracor 700) produced commercially have a high sensitivity and a small internal volume, so that they can be used with capillary gas-chromatographic columns and coupled with another detector, for example an FID.[1,114,115] The advantage of the latest model (700 A) over the earlier model is that it can be tuned for the selective detection of any of the following classes of substance: halogen-, sulphur, and nitrogen-containing compounds, hydrocarbons, and nitrosamines.[115]

The main parts of the ECD are the reactor with the furnace for converting the substances being analysed into the compounds detected; the absorber, in which the reaction gases are brought into contact with the solvent (de-ionised water, alcohol, or a suitable mixture); the separator for separating the solution from the insoluble gases; the cell for measuring the electrical conductivity; the system for circulating and regenerating the solvent; and electronic circuits for controlling the temperature of the reactor furnace and for measuring the electrical conductivity of the solution in the cell. In the 700 A model,[112] the reactor consists of a nickel capillary, which acts simultaneously as the catalyst; a quartz capillary can also be used. A scrubber is placed between the reactor and the measuring cell to extract interfering components from the mixture of decomposition products. The use of a bipolar pulse voltage, applied to the electrodes in the 700 A model (the duration of the pulses is one tenth that of the intervals between them) makes it possible to avoid such undesirable phenomena in the electrical conductivity measurement as polarisation of the electrodes, the capacity effect, and heating of the cell.

The magnitude of the ECD signal is determined primarily by the concentration of the product being recorded in the cell, its dissociation constant in the solvent, and the equivalent ionic conductivity due to the cations and anions. Selectivity of action is achieved by the correct choice of chemical decomposition reaction and absorption conditions, under which the required product is readily soluble and readily dissociated to give ions, while other substances either are insoluble in the solvent used or do not ionise in it.[1]

In the analysis of sulphur-containing compounds, the optimum conditions correspond to the combustion of the substance in oxygen or air at 800 °C in a nickel reaction tube with the use of pure methanol as electrolyte.[112,114,115] The hydrogen chloride which may be obtained from chlorine-containing impurities is removed in the scrubber by the action of silver; oxides of carbon are sparingly soluble in the alcohol, and their quantity is also restricted by removing the excess of solvent before introduction into the reactor. The yields of soluble oxides of nitrogen (from possible traces of nitrogen-containing compounds) are slight under these thermal decomposition conditions.

For the detection of nitrogen-containing compounds, the optimum conditions correspond to the reducing version; with decomposition in a nickel reactor, all nitrogen-containing compounds are detected, but when a quartz or gold reaction tube is used, nitrosyl compounds can be determined selectively.[1] The electrolyte in the absorber consists of a mixture of water and n-propanol (1:1). Hydrogen chloride and hydrogen sulphide obtained from chlorine- and sulphur-containing impurities are removed in the scrubber by the action of a suitable base; the ionisation constant of methane is too low, and it does not give a signal.

In the analysis of halogen-containing compounds using the ECD under both oxidising and reducing conditions, the hydrogen halide is formed, but reduction in a quartz tube at 800–900 °C gives a more favourable composition for the side products, which does not require the use of a scrubber.[1]

The molar signal of the ECD is directly proportional to the number of corresponding heteroatoms in the molecule of the substance being analysed, so that the ECD is particularly sensitive to compounds containing a large number of sulphur, halogen, or similar atoms. The detection limit is $(2–4) \times 10^{-12}$ g s^{-1} for N-containing compounds, 2×10^{-12} g s^{-1} for S-containing compounds, and 5×10^{-13} g s^{-1} for Cl-containing compounds, calculated for the heteroatom; the linear range is 10^4 for N- and S-containing compounds, and $10^5–10^6$ for Cl-containing compounds. The selectivity with respect to hydrocarbons is $10^5–10^6$.[1]

The ECD has been used successfully for the gas-chromatographic analysis of hydrogen sulphide and sulphur dioxide in air[108,112] and natural gas,[1] nitrogen- and sulphur-containing compounds in petroleum products,[114] nitrosamines, pesticides with a high sulphur content (malathion, parathion, trithion, etc.), polychlorinated biphenyls and other chlorinated insecticides in natural materials at the level of several nanograms or below in the specimen.[1,112,115]

5. Detectors Based on Electron Capture

The action of a group of selective gas-chromatographic detectors — electron-capture, aerosol-ionisation, plasma chromatographic, and mas-spectrometric with chemical ionisation — is based on similar ionisation processes, chief of which is the capture of thermal electrons by the molecules of the substances being analysed. In the first two detectors, the useful signal is the change in the concentration of electrons in the measuring cell at the moment when the substance being analysed passes through, and in the other two detectors the composition and properties of the ions formed are studied. The plasma chromatograph records the spectra of the mobility of the ions, and the mass spectrometer with chemical ionisation analyses the composition of the positive or negative ions.

The source of the electrons in these detectors is most frequently the β-radiation of radioactive elements (for example tritium or ^{63}Ni). The energy of the electrons of the β-rays, equal to 17.6 keV for tritium and 67 keV for ^{63}Ni, is too high to ensure the electron capture mechanism; the energy is lowered by flushing the ionisation compartment with a suitable carrier gas, which has a high electron affinity and a high

ionisation potential; this gas may be nitrogen, noble gas (argon, helium) containing 5–10% methane, and other gases and mixtures. As a result of elastic and inelastic collisions with the atoms and molecules of the carrier gas at atmospheric pressure, the electrons of the β-radiation lose their excess energy until their energy becomes suitable for reactions giving ion pairs: positive ions from the molecules (or atoms) of the carrier gas, and low-energy electrons (0–10 eV).

Other reactions may take place in parallel between electrons, ions, and neutral species (additives in the carrier gas, impurities, etc.). By selecting the carrier gas, its pressure, the magnitude and character of the voltage at the electrodes, the temperature, the velocity and direction of the flushing gas, and the design of the ionisation compartment, it is possible to achieve the required distribution of electrons with respect to energies in these detectors and to create conditions for particular ionisation reactions in them.

6. The Electron-capture Detector

The principles of the operation and practical application of the electron-capture detector (ECpD), which is the most widely encountered selective gas-chromatographic detector, have been examined in detail in many papers, monographs, and reviews.[1–3,44,110,116–128] Recent work has involved a detailed study of the mechanism of the reactions taking place in the ECpD and the production of the signal, and the search for ways of increasing the selectivity and sensitivity, extending the linear range, decreasing the volume, and optimising the design and operating conditions.

The theory of the ECpD[1,118,119] is based on the idea of an ideal-mixing reactor; it is assumed that the current of the detector is due entirely to electrons; the latter may disappear as a result of capture by the molecules of the substances being analysed and by recombination with positive ions, and also as a result of the wall effect and flushing.

According to Ref. 117, the magnitude of the measured current is determined not only by the electron density but also to a large extent by the field of the negative ions, which are localised close to the cathode under the influence of the counter current of the flushing gas.

New data on the composition of the ions and their behaviour inside the ECpD, obtained using a mass-spectrometric detector with chemical ionisation (MSCI),[122,129] plasma chromatography (PC),[130,131] and a system of two ECpD connected in series and operating under different supply conditions,[126] show better agreement with the field theory of electron-capture detection. In particular, it has been suggested that in the detector there is a centrally located zone of electrons; under pulse supply conditions, this zone becomes broader with increase in the time interval between the pulses, and during the pulse all the electrons leave the cell. In some cases it has been possible to estimate the contributions of the space charge of the negative ions[126] and the current created by the selective migration of positive ions[128] to the recorded ECpD signal.

The molar ECpD signal increases with increase in the number of atoms or functional groups with an electron affinity in the molecule of the substance being analysed, and a synergistic effect is observed when a certain number has been reached. This feature, and also the tendency for the relative sensitivity to be influenced by various factors such as the presence of impurities in the carrier gas, the electric field potential, the temperature of the detector, etc., make it difficult to carry out the theoretical calculation of the relative molar sensitivity coefficients, so that it is necessary to calibrate the detector in each specific case, although a whole series of correlations exists.[121,132,133]

A study of the influence of traces of oxygen in the carrier gas on the sensitivity of the ECpD with respect to various chlorinated hydrocarbons showed that the addition of 0–3.5% oxygen to the carrier gas leads to a sharp increase in the intensity of the signal of monochloroalkanes,[134] whereas the signal from polychlorinated hydrocarbons changes little. An increase in the sensitivity in the presence of oxygen has also been detected for dichloromethane,[136] carbon dioxide,[135] and polycyclic aromatic and related hydrocarbons,[137,138] and the difference in the magnitude of the signals obtained in the presence and in the absence of oxygen can be used, for example, for the qualitative identification of the structural isomers of polycyclic aromatic hydrocarbons in air.[138] Sensitisation of the ECpD is also observed when N_2O is added to the carrier gas.[139–142] This was attributed to reversible reactions of O_2 and N_2O with slow electrons, leading to the formation of the negative ions O_2^-, O^-, NO^-, etc., and if the substance can react with these species to give stable secondary negative ions, its appearance in the detector in fact leads to a decrease in the electron concentration, that is to the appearance of a signal.

An ECpD signal can be obtained from normal saturated hydrocarbons by increasing considerably the electric field by raising the voltage at the electrodes and using highly pure argon as carrier gas. With increase in the kinetic energy of the electrons, there is a change in the ionisation mechanism (use of the Penning effect).[143] These techniques lower the selectivity of the ECpD in the general sense, but they may be useful for solving particular problems, for example for determining Kovacs indices.[139,143] Usually, however, in the determination of retention indices in work with the ECpD, the standards used are some homologous series of electron-acceptor substances, such as esters of trichloroacetic acid[144] and n-bromoalkanes;[145] the latter have also been recommended for standardising the ECpD signal in quantitative analysis.

The introduction of electron-acceptor substituents into the molecule of the substance being determined is widely used to increase the sensitivity of the ECpD.[1,146] For example, the replacement of the chlorine atom in the methyl chloride molecule by an iodine atom leads to an increase in the signal by a factor of 10^4 with a methyl iodide detection limit of 3.1×10^{-14} g; the detection limit for N,N'-dipentafluorobenzoylpentafluoroaniline is 1.6×10^{-19} mole ($\sim 10^{-16}$ g).[147] The introduction of electrophors, however, should not lead to a significant decrease in the volatility of the substance, hindering its analysis.

Examples of the use of gas chromatography with an ECpD include the determination of micro-quantities of peroxyacetyl nitrate,[148] the chlorides of phosphorus, silicon, tin, and germanium, sulphur hexafluoride, phosphine, etc.[149] in air; 2,4-dichlorophenol and various forms of hexachlorocyclohexane in soil and plants;[150] and water in solvents.[151] The improvement of the design and the optimisation of the operating conditions of the ECpD have made it possible to extend the linear range to $(1–5) \times 10^3$,[152] improve the stability,[153, 154] decrease the volume, and use the ECpD in combination with capillary columns.[155,156] A method has been proposed for purifying a solvent (n-pentane) from contaminants which give a signal with this detector.[157]

7. The Aerosol-ionisation Detector

The action of the comparatively new aerosol-ionisation detector (AID) is based on the formation of large aggregates of molecules of the substance being analysed and some reagent, in order to increase their ionisation cross-section

when the ECpD is used.[158–160] AID models in which the processes of aerosol formation and ionisation either take place in different compartments[159] or are combined in a single compartment[160] have been described. The concentration of the reagent for generating the aerosol in the carrier gas (air) is 10^{-2}–10^{-3} vol.%. This gives sol particles containing tens of molecules. The temperature of the detector is determined by the stability of the aerosol used.

The development of the theory of this method has made it possible to calculate the minimum detectable quantity of substance from data on the values of the saturation current, the coefficient of adhesion of the ions to the aerosol particles, and the number of aerosol particles per unit volume.[159,160] The AID is selective and sensitive with respect to halogen-containing hydrocarbons, amines, organometallic compounds, SO_2, SO_3, NO_2, etc.[159,160] The reagents for the formation of the aerosol particles are selected with allowance for the chemical properties of the substances being analysed; trifluoroacetic acid is used for compounds with basic properties, and amines for acidic compounds; halogen-containing hydrocarbons are passed over heated copper oxide, and organometallic compounds are subjected to thermal decomposition. Additional reactions are also used to convert the substances being analysed into strong acids or bases, for example SO_2 into SO_3 with subsequent reaction with an amine. The linear range for all substances is 10^2; the limit of detection for different groups of substances varies in the range 10^{-11}–10^{-10} g s^{-1}.[158–160]

8. Plasma Chromatography

The name itself of this detector reflects the principle of its operation: in it, the plasma formed by the ionisation of the molecules of the substance being analysed is separated, and the ratio of the ions present in it is determined; this is essentially analogous to chromatography.[130,131,161–166]

The mechanism of operation and the fields of application have been reviewed.[161] The original ions are generated as a result of the interaction of the molecules of the carrier gas (purified nitrogen or air containing water vapour) with electrons, the source of which is ^{63}Ni foil. In the carrier gas (nitrogen), the positive nitrogen ions formed initially react with water molecules to give the ions NH_4^+ and NO^+ and the cluster ions $(H_2O)_nH^+$, $(H_2O)_nNO^+$, etc. When the carrier gas is air, the negative ions O_2^-, O_4^-, $(H_2O)_nO_2^-$, CN^-, CO_3^-, and CNO^- are also formed.[130,131,161,162,166] The relative concentration of the ions and their degree of hydration depend on the concentration of water vapour and on temperature. In addition to ions, the PC ionisation compartment also contains electrons with an energy of ~0.5 eV.[131,161,162,164]

The molecules of the substances being analysed enter the ionisation compartment and interact with the above ions and electrons to give new quasi-molecular and simple dissociative ions. The mixture of ions and carrier gas is directed for separation into a drift tube (usually by pulses of duration 0.25 ms at time intervals of 0–20 ms). The drift tube is flushed continuously with an additional counter current of gas (nitrogen, air, sulphur hexafluoride) at atmospheric pressure. The rate of movement of the individual ions in it, and in some cases the composition of the ions[162,166] depend not only on their mass and charge and the field intensity (as in the analyser of the mass spectrometer) but also on the size of the ions and on the mass, size, and polarisability of the molecules of the drift gas. The successive recording of the ions at the outlet from the drift tube gives the spectrum of their mobility, characteristic for each substance. To observe the mobility of large ions, it is preferable to use a drift gas with a high molecular mass, such as sulphur hexafluoride.[162]

The mobility spectra of ions with a mass of up to 400 are usually obtained in 20 ms. They are recorded using digital signal averagers, which make it possible to carry out the summation of several thousand such spectra in several minutes and present them in convenient form. The spectra are interpreted by comparing them with the spectra of the individual compounds, obtained under the same conditions, and also by comparing them with analogous spectra obtained by the MSCI method.[161,162]

PC is specially designed for the analysis of tracer quantities of materials (10^{-8}–10^{-14} g) and is more sensitive than, for example, the FID. Large specimens overload the detector, and as a result of secondary reactions the interpretation of the spectra is difficult. An important feature is that PC makes it possible to obtain the spectra of the mobility of positive and negative ions, and this makes it more informative. The ratio of the intensities of the spectra of the positive and negative ions provides an additional specific characteristic of a substance.

As in the sensitised ECpD, in PC the negative ions are formed only by substances which are electron acceptors, and the spectrum of the mobility of the negative ions makes PC selective with respect to the same classes of compound. There are both associative and dissociative mechanisms for the addition of an electron.[131,161] Thus monohalogeno-derivatives of aromatic hydrocarbons undergo dissociative splitting, and nitrobenzene shows only associative interaction, giving a negative molecular ion, whereas the halogen derivatives of nitrobenzene and nitrotoluene react by both mechanisms. There is a correspondence between the PC and MSCI data with identical reaction gases for alkanes, halides, nitroaromatic compounds, etc.[161] At the same time, these methods show appreciable differences. One of these is the ease of formation of the groups of ions M_2H^+ and M_3H^+ by polar substances (alcohols, esters, etc.[161]) in PC.

PC has been used for the qualitative identification of alcohols, alkyl halides, substituted and polynuclear aromatic compounds, aliphatic N-nitrosamines, and pesticides, various isomers of fluorotoluenes and picolines, and the methyl esters of toluic and phthalic acids.[131,161,165] There are as yet comparatively few published data on quantitative analysis.[130,161]

9. Mass Spectrometry with Chemical Ionisation

The combination of a gas chromatograph with a mass spectrometer and a computer is widely used to identify substances in complex multi-component mixtures, and various countries now produce standard commercial instruments: chromatograph–mass–spectrometers, fitted with libraries of mass spectra and computers.[44,167,168] Like the Fourier transform infrared spectrometer, the chromatograph–mass–spectrometer can act as a universal detector if the chromatogram is recorded with respect to the total ion current, or as a selective detector, if only ions with definite masses are recorded. MSCI at a low pressure ($\leq$ 1 mmHg) and at atmospheric pressure makes it possible to combine the fast action and informative character of mass spectrometric technique with the selectivity of detectors based on ion–molecule and electron–molecule interactions.[169–176] The spectra obtained by MSCI for the most part contain the peaks of the molecular ions and fragments of the molecules being analysed, which are simpler than the ions formed in the ordinary mass spectrometer as a result of the bombardment of the specimens by electrons in a high vacuum. It is possible to record the spectra of the positive and negative ions separately.

The selectivity of MSCI, as in the case of PC and the sensitised ECpD, can be controlled by creating the necessary set of working ions and electrons in the ionisation compartment

by appropriate selection of the source of primary electrons, the carrier gas (most frequently nitrogen), and the reagent gas (methane,[167,172] oxygen,[173,174] oxygen and methane,[175] ammonia,[176] etc.). The source of electrons in MSCI is ^{63}Ni at atmospheric pressure,[169,173,174] and a heated rhenium cathode at low pressure.[170,171,175,176] The composition of the working ions in the ioniser also depends on the concentration of traces of water and other substances in the gases used and on temperature.[130,169] The normal operation of the mass analyser in MSCI requires powerful vacuum pumps (for example two pumps with a speed of 800 litre s^{-1} are used simultaneously.[173])

MSCI combined with capillary gas-chromatographic columns has been used to analyse micro-quantities of aliphatic alcohols[172] and also polychlorinated and polybrominated benzenes in foodstuffs.[173–175] It is possible to determine selectively the most toxic 2,3,7,8-tetrachlorobenzo-*p*-dioxin in the presence of a large number (21) of isomers of this compound and other related substances.[174] The successive use of NH_3 and ND_3 as reaction gas made it possible to identify primary, secondary, and tertiary amines in a complex mixture of hydrocarbons and nitrogen-containing compounds (from the increase in the mass of the deuteriated molecular ion in the spectrum of the positive ions, compared with the protonated ion).[176]

MSCI is used mainly for the qualitative identification of substances in complex mixtures. The minimum detectable quantities of the substances being analysed is 10^{-9}–10^{-12} *g*.[169,172,174] Together with mass spectrometry, MSCI is also used to study the composition of the ions in other detectors (ECpD, PC, AID, and SID) to obtain a deeper understanding of the mechanisms of ionisation in these detectors and to determine the optimum conditions for their operation.[94,130,161,162]

IV. SOME CHARACTERISTIC FEATURES OF WORK WITH SELECTIVE GAS-CHROMATOGRAPHIC DETECTORS

The use of selective detectors raises a number of specific problems. One concerns qualitative analysis from the Kovacs indices, since almost all selective detectors are insensitive to n-paraffins, which provide a series of standards in this identification system. The introduction of phosphorus, sulphur, halogen, and other indices, and the use of reaction gas chromatography, are helping to solve this problem.[145,177,178] To increase the reliability of identification, selective detectors are often used in combination with universal detectors.[23,179–182] Success in these cases is to a large extent determined by the quality of the connections.[183,184]

The fields of application of many selective detectors overlap; for comparison of their data, it is proposed that selectivity coefficients for selected substances be normalised under standard conditions.[183]

The principal requirements to be satisfied by the gas-chromatographic system in work with highly sensitive selective detectors reduce to the use of thermally stable materials and sorbents, which do not contain elements or groups to which the given detector is sensitive. Dexsil 300, SE-30, OV-225, and other silicones, PEG-20000, and Versamid-900, deposited in small quantities on silanised inert carriers, are used as stationary liquid phases. Concentration is carried out using porous polymers and graphitised carbon black. Increased demands are made on the purity of the gases used.

Selective gas-chromatographic detection is now at the stage of intensive development. The appearance of fundamentally new methods has been accompanied by the revival of older and simpler methods on the basis of new techniques using new materials. The possibilities opened up by the use of selective detectors for the gas-chromatographic control of pollution in the environment are acquiring particular importance in connection with the improvement of measures for its protection.

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Institute of Catalysis,
Siberian Branch,
Academy of Sciences of
the USSR, Novosibirsk